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A thermal and X-ray investigation of scarbroite.

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Summary.—Scarbroite, a fine-grained but compact deposit obtained from fissures in the sandstone on the north Yorkshire coast, is shown by chemical analysis to have an idealized formula $Al_2(CO_3)_3.12Al(OH)_3$. X-ray and electron diffraction data indicate a triclinic cell with a 9·94 Å., b 14·88 Å., c 26·47 Å., α 98·7°, β 96·5°, and γ 89·0°. A layer structure consisting of gibbsite-type sheets of $Al(OH)_3$ and sheets of $Al_2(CO_3)_3$ is proposed. The structure is stable from room temperature to about 125° C.

In a preliminary report (Duffin and Goodyear, 1957), the authors described an aluminous mineral obtained from vertical fissures in the sandstone in South Bay, Scarborough. In spite of some quantitative difference between the properties of this mineral and those of scarbroite as first announced by Vernon (1829), some later measurements on specimens of the original material by Melmore (1930) show excellent agreement with the corresponding data in this paper (p. 354): there seems no doubt that the two are identical.

There appear to have been no other investigations of the mineral, although the American Petroleum Institute research project no. 49 on clay minerals (1951) states, without evidence, that it is probably a mixture of clays. The present paper is an extension and amplification of the preliminary report, and confirms Vernon's hypothesis that scarbroite is a mineral in its own right.

Occurrence and appearance. Specimens appear to be localized in a small cove just south of South Bay, where vertical fissures in the sandstone are occasionally lined with dark brown and grey materials between which the scarbroite is sandwiched. Many specimens of scarbroite are veined with light-brown material, which is largely gibbsite, and most of them also contain varying amounts of quartz. It has proved possible,

however, to obtain specimens from layers about $\frac{1}{2}$ inch thick that show no impurity lines in X-ray photographs, although inevitably some quartz and possibly gibbsite may be present. The darker materials sandwiching the scarbroite are largely discoloured quartz, although the grey material contains some kaolinite and calcite, and X-ray photographs of it show a few lines that are not identifiable.

The scarbroite itself, when relatively pure, is white and compact, but most samples are soft and easily crumbled into a very fine-grained powder. The ease with which the mineral crumbles may be due to continual wetting by surface water from the cliff top, since a few dryer specimens are much harder.

Physical and chemical data. Scarbroite is too fine-grained for detailed optical study, but a mean refractive index of 1·509 was obtained. Melmore (1930) states that the refractive index is less than 1·509 and very slightly greater than 1·502. Determinations of the specific gravity in the lump, both by pycnometer and displacement methods, yielded variable results whose mean was 1·85. Using powdered material to eliminate entrapped air as far as possible, a partially evacuated pycnometer gave 2·03, while flotation in a methylene iodide–ethyl iodide mixture gave $2{\cdot}01 \pm 0{\cdot}01$, a result which is probably the most reliable. These results are in good agreement with Melmore's value of 2·05 determined by flotation.

The particle size of the material as found is sufficiently small to give continuous X-ray powder reflections, and electron micrographs (see following note by G. W. Brindley and J. J. Comer) show that the crystallites have a plate-like habit and average about 1 μ across their basal planes.

A chemical analysis was carried out by Dr. R. A. Chalmers of the University of Aberdeen, and gave: SiO_2 3·2 %, Al_2O_3 45·7 %, MgO 0·1 %, Na_2O 1·7 %, K_2O 0·2 %, H_2O 37·9 %, SO_3 1·8 %, CO_2 7·9 %, total 98·5 %. In three analyses Melmore found SiO_2 6·48, 5·69, 5·88 %, Al_2O_3 44·19, 44·32, 44·02 %. The only cation present in amounts sufficient to be associated with the CO_2 is Al^{3+} and this suggests that the mineral is a basic aluminium carbonate. If the silica is attributed to free quartz and the minor constituents (each contributing less than 2 %) are associated with contaminants then the empirical formula would be $Al_2(CO_3)_3.12{\cdot}9\ Al(OH)_3.15{\cdot}6\ H_2O$. The 15·6 H_2O in the formula amounts to 17·0 % of the original material and accounts for the loss in weight when a sample is heated to about 100° C. without a noticeable structural change as revealed by X-ray powder data. It is also possible that a

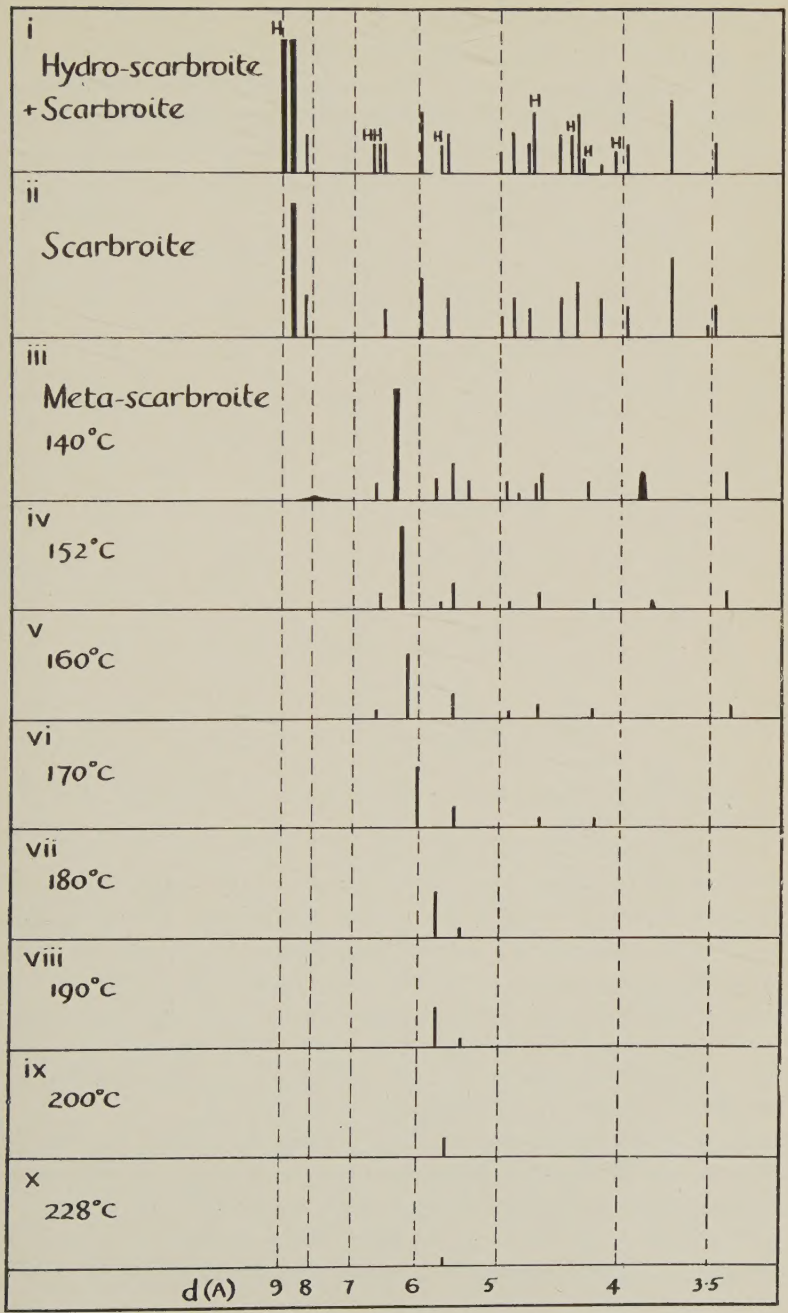

FIG. 1. X-ray powder patterns of hydroscarbroite, scarbroite, and metascarbroite. Heights of lines represent relative intensities estimated visually (compare Tables I and II).

small amount of gibbsite impurity was associated with the sample that was analysed, even though no gibbsite reflections were recorded in its X-ray powder pattern. If an allowance were made for this, the idealized formula of the material in equilibrium with the atmosphere in the

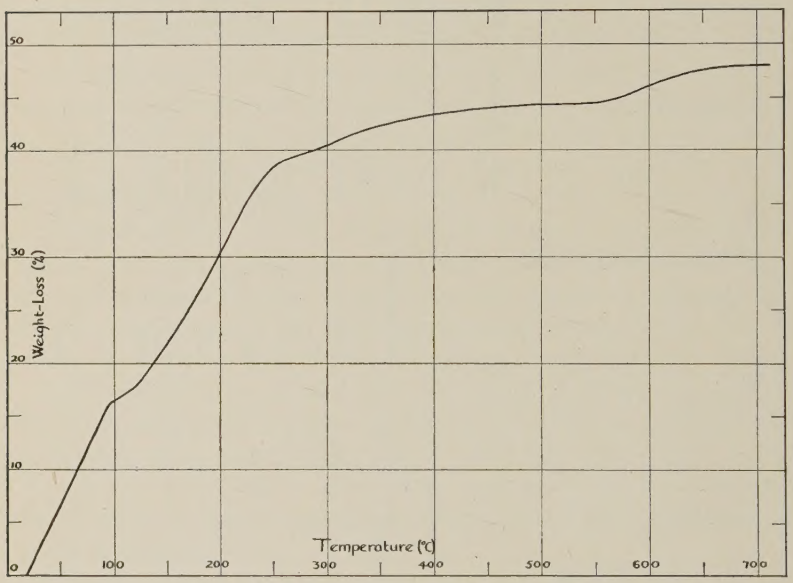

Fig. 2. Weight-loss curve for scarbroite.

range room temperature to 100° C. (see p. 358) may well be $Al_2(CO_3)_3.12\ Al(OH)_3$.

Thermal and X-ray data. The effect of heat-treatment on scarbroite was studied by heating a sample to constant weight at predetermined temperatures and taking X-ray powder photographs of the material after it had cooled quickly to room temperature. The weight-loss curve obtained is shown in fig. 2, the loss being expressed as a percentage of the material as found. The X-ray photographs were taken with monochromatized Cu-$K\alpha$ radiation, mostly with a Guinier-type transmission camera of effective diameter 22·9 cm.; calibration was effected by mixing aluminium powder with the specimen to be X-rayed.

Prior to any heat-treatment, when a lump of scarbroite was lightly crushed and an X-ray photograph taken immediately, the diffraction pattern obtained was that shown in table I, column i, and in fig. 1, i. The reflections marked H in the figure varied in their intensity from specimen to specimen, but if the powder was left exposed to the atmo-

TABLE I. Powder patterns of scarbroite and hydroscarbroite.

i Hydroscarbroite +scarbroite.		ii Scarbroite.		i Hydroscarbroite +scarbroite.		ii Scarbroite.		i Hydroscarbroite +scarbroite.		ii Scarbroite.	
I.	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.
vvs	9·00			wm	3·005	vw	3·011	vw(b)	1·984	w	1·994
vvs	8·74	vvs	8·66	m(b)	2·981	wm	2·986	f	1·969	w(b)	1·969
wm	8·35	m	8·34	w(vb)	2·922					vw	1·945
wm	6·77			vw	2·864	w	2·864	vw	1·932	w	1·929
wm	6·69			tr	—	w	2·823	f	1·914		
wm	6·59	wm	6·56	tr	—			f	1·903	vw	1·903
w	5·99	ms	5·99	vw	2·801			f	1·873	w	1·871
wm	5·72			tr	—			w	1·855	w	1·852
vw	5·62	m	5·63	w	2·752	w(b)	2·750	vw	1·841		
wm	5·00	w	5·01	w	2·704	vw	2·703	w	1·825	wm	1·825
vw	4·900	m	4·906	w	2·674			w(b)	1·785	f	1·794
m	4·739	wm	4·747	tr	—	w(b)	2·632	vw	1·776	w	1·776
m	4·713			vw	2·602	vw	2·600	f	1·762	vw	1·760
ms	4·467	m	4·456	w(b)	2·552	w(b)	2·560	vw	1·746		
m	4·386			vw	2·501	vw	2·498	w(b)	1·698	f	1·703
m	4·349	ms	4·331	vw	2·477	vw	2·475	tr	—	vw	1·629
vw	4·291			m(b)	2·447	w	2·447			w	1·610
Tr	—	m	4·159	vw	2·426			tr	—	w	1·593
w	4·074			f	2·405			f	1·534	vw	1·560
m	3·985	wm	3·973	wm	2·365	wm	2·366	tr	—	f	1·484
ms	3·726	s	3·724	w	2·338			tr	—		
		vw	3·533			f	2·280	vw	1·471	w(vb)	1·474
m	3·482	wm	3·491	vw	2·226	w(b)	2·222	ms	1·452	m	1·452
w(b)	3·279	f	3·286	w	2·207	vw	2·162	m	1·437	vw	1·418
w(b)	3·253	w	3·252	vw	2·148	wm	2·149	vw	1·389		
tr	—	f	3·187	vw	2·138	w	2·137	f	1·380	w	1·381
wm	3·130	f	3·129	wm(b)	2·099	vw	2·089	tr	—		
vw	3·064	f	3·092	w(b)	2·075	w(b)	2·072	tr	—		
tr	—	w	3·039	f	2·053			m	1·167		

sphere for several weeks and then photographed the H-reflections were no longer recorded and the pattern was that displayed in fig. 1, ii, the reflections corresponding very closely to the unlabelled reflections of fig. 1, i. Powder patterns of the material at intermediate stages in the transition showed the process to be a continuous one, the H-reflections becoming fainter with a corresponding strengthening of the other reflections.

It thus appears that in the material as found two phases may exist, one (for which the name *hydroscarbroite* is proposed) spontaneously dehydrating to the other (scarbroite) when the material is left to come into equilibrium with the humid atmosphere at room temperature. The dehydration process can be hastened by heating the material; for example, hydroscarbroite can be completely transformed by heating at 40° C. for 1 to 2 hours. It seems that the change is completely irreversible since no specimens composed entirely of hydroscarbroite have been found, nor have attempts to transform scarbroite to hydroscarbroite been successful.

Fig. 2 shows that the loss in weight of the material varies uniformly

with temperature up to 100° C., at which temperature the curve flattens out somewhat and then begins to rise steeply again at about 125° C. The X-ray powder pattern shows only very minor changes over this temperature range, suggesting a stable scarbroite phase from room temperature to 125° C. If the loss at 100° C., i.e. 16·5 %, is regarded as free water then the chemical formula for scarbroite is probably $Al_2(CO_3)_3.12\ Al(OH)_3$ as previously suggested.

At 130° C. the scarbroite powder pattern disappears, to be replaced by one completely different. This indicates a reconstruction of the crystal lattice to form a further modification for which the name *metascarbroite* is appropriate. At higher temperatures, up to about 230° C., the X-ray pattern shows a continuous shift of some lines to higher Bragg angles together with a progressive decrease in their intensity and a corresponding increase in their diffuseness. These changes in the powder pattern are illustrated in fig. 1, iii–x, and the spacings of the reflections given in columns iii to x in table II. Above 230° C. the

TABLE II. Powder patterns of metascarbroites.

iii 140° C. 28 hrs.		iv 152° C. 22 hrs.		v 160° C. 24 hrs.		vi 170° C. 30 hrs.		vii 180° C. 3 days		viii 190° C. 3 days		ix 200° C. 2½ days		x 228° C. 2 days	
I.	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.	*I.*	*d*, Å.
f(b)	8·09														
vw	6·73	vw	6·62	f	6·72										
vs	6·41	s	6·25	ms	6·17	ms	6·04	m	5·76	wm	5·76	w	5·64	f	5·63
f	6·13														
w	5·77	f	5·71												
m	5·57	wm	5·54	wm	5·55	w	5·55	f	5·47	f	5·45				
w	5·38	f	5·23												
w	4·95	f	4·93	f	4·93										
f	4·84														
w	4·69	tr	—												
wm	4·65	w	4·64	w	4·66	f	4·64								
w	4·26	f	4·22	f	4·22	f	4·20								
wm(b)	3·89	f	3·83												
wm	3·45	vw	3·43	vw	3·41										
f	3·30														
vw	3·21														
f	3·17														
wm	2·96	f	2·95												
f(b)	2·78														
wm(b)	2·59	f	2·60												
wm	2·539	vw	2·529	wm	2·529	w	2·512	f	2·484	f	2·486	f	2·459		
f	2·475														
f	2·432														
w(b)	2·351														
s	2·199	m	2·192	m	2·192	m	2·181	w	2·164	w	2·164	vw	2·142		
f	2·128														
w(b)	2·031														
tr	—														
tr	—														
w	1·478	w	1·450												
ms(b)	1·441	m	1·439	m	1·434	wm	1·427								
m(b)	1·406	w	1·402												

X-ray pattern becomes so diffuse that no measurable lines remain, although at 900° C. a very diffuse pattern of γ-Al_2O_3 emerges.

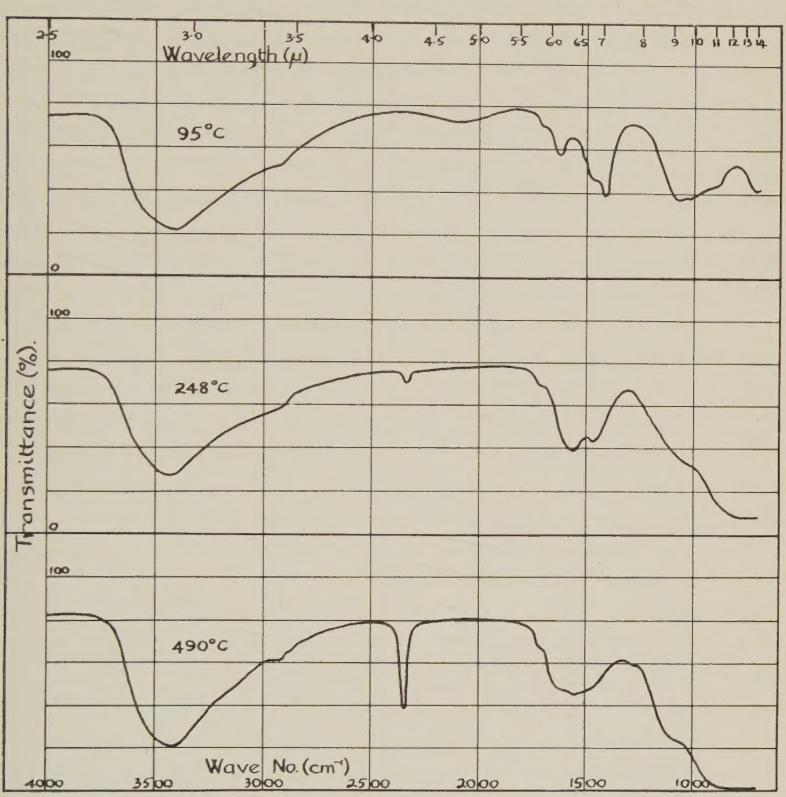

FIG. 3. Infra-red absorption curves for scarbroite after being heated at 95° C., 248° C., and 490° C. No precaution was taken to prevent water being adsorbed on the crystallite surfaces after the heat-treatment.

Immediately above 100° C. further loss in weight with increase of temperature is undoubtedly due to the loss of hydroxyl groups, and if this were the only change occurring, all the hydroxyl would have been lost at 245° C. In fact the weight-loss curve does flatten out at about this temperature. Any further loss at higher temperatures would then be due to the breakdown of the carbonate in the lattice with the evolution of CO_2. The loss of CO_2 is confirmed by infra-red absorption curves shown in fig. 3; these were taken for scarbroite which had been heated at 95° C., 248° C., and 490° C. At 490° C. the presence of a peak at

2350 cm.$^{-1}$ shows quite clearly the presence of molecular CO_2 occluded in the specimen, but the small peak in the trace from the specimen heated at 248° C. shows that a few carbonate groups had broken down even at this lower temperature. It is thus reasonable to suppose that the carbonate begins to break down at temperatures just below 250° C. and that the discontinuity in the weight-loss curve at about 250° C. marks the beginning of the loss of CO_2 by the specimen. At 500° C., when the curve flattens out again, the total loss is about 44 % compared with 45·8 % attributable to the H_2O and CO_2 in the analysis. The extra loss of 4 % on heating to even higher temperatures is probably due to the loss of CO_2 gas occluded in the specimen together with a breakdown of the sulphate impurity in the material.

Structural considerations. X-ray photographs of scarbroite, taken with a Brindley-type semi-focusing camera, of specimens oriented by deposition from suspension in water showed enhancement of the 8·66 Å. and 4·33 Å. reflections. These are clearly basal reflections and indicate that d_{001} is some multiple of 8·66 Å. In the absence of single crystal data an attempt was originally made to index the scarbroite powder pattern using a Bunn chart, and a relatively satisfactory fit could be obtained in terms of a large hexagonal cell with a 34·5 Å. and c 17·3 Å. (see Duffin and Goodyear, 1957).

Subsequently, electron diffraction photographs taken by Brindley and Comer (see following note) showed that the a^*–b^* plane of the reciprocal lattice was only pseudo-hexagonal and provided the following values for the parameters: d_{100} 9·90±0·02 Å., d_{010} 14·67±0·04 Å., and γ^* 90°±0·05°. This suggests that the unit cell is either orthorhombic or of lower symmetry. However, it was found impossible to explain the X-ray reflections with an orthorhombic cell with the values of a and b suggested by the electron diffraction data. Perhaps this was to be expected since if the structure of scarbroite is in some way related to that of gibbsite (which is reasonable in view of the close association of these minerals both in environment and composition) it seems unlikely that the presence of a small amount of $Al_2(CO_3)_3$ would raise the symmetry from monoclinic to orthorhombic.

In seeking a cell of lower symmetry to explain all the diffraction data two pieces of evidence proved invaluable: Diffractometer records of scarbroite (G. W. Brindley, private communication) showed a trace reflection at 27±1 Å., which suggests that the strong basal reflections at 8·66 Å. and 4·33 Å. are 003 and 006 respectively giving a d_{001} of 26 Å. And the ease with which clear and extensive electron diffraction patterns

were obtained suggests that the c-axis is nearly perpendicular to the (001) face of the crystal.

Assuming initially $d_{001} = 26$ Å. together with the values of the reciprocal lattice parameters a^*, b^*, and γ^* found by Brindley and Comer and in the absence of a reasonable monoclinic fit, a triclinic cell was found which accounted very well for the X-ray diffraction data. The parameters of this cell are a 9·94 Å., b 14·88 Å., c 26·47 Å., α 98·7°, β 96·5°, and γ 89·0° and the values of the 100, 010, and 001 spacings are 9·88 Å., 14·71 Å., and 25·99 Å. respectively. Although slight adjustments had to be made to Brindley and Comer's values of a^* and b^*, the cell still explains the electron diffraction data within the expected limits of accuracy. The agreement between the Bragg angles of the observed X-ray reflections and those calculated for the above cell is shown in table III; for every reflection the discrepancy between the observed and calculated values of θ is within the limits of the experimental error.

TABLE III. Observed and calculated θ°_{Cu} for scarbroite.

$\theta_{obs.}$	$hkl.$	$\theta_{calc.}$	$\theta_{obs.}$	$hkl.$	$\theta_{calc.}$
5·104°	003	5·104°	9·962°	202	9·970°
5·306	$10\bar{2}$	5·315	10·253	006	10·250
6·743	$11\bar{3}$	6·746	10·682	$20\bar{4}$	10·677
7·398	$\bar{1}13$	7·406	11·189	025	11·190
7·865	014	7·859	11·944	222	11·944
8·853	$1\bar{2}3$	8·861	12·604	$23\bar{1}$	12·592
9·041	030	9·044	12·757	$14\bar{2}$	12·756
9·345	201	9·333			

Assuming the chemical formula for scarbroite to be $Al_2(CO_3)_3$. 12 $Al(OH)_3$ and taking 4 molecules per unit cell, the calculated density is 2·03 as compared with an observed value of 2·17 for scarbroite after being heated to 100° C. to remove externally absorbed water. It is tempting to postulate a layer structure for scarbroite consisting of $Al(OH)_3$ layers as found in gibbsite between which are situated layers of $Al_2(CO_3)_3$. One gibbsite-type layer of area approximately equal to the (001) face of the scarbroite cell would contain 12 $Al(OH)_3$, so that four such layers would account for all the $Al(OH)_3$ in the cell. If these layers were parallel to the (001) face and were stacked as they are in gibbsite (Megaw, 1934) their total thickness would be $\sim$ 19·5 Å. leaving a space $\sim$ 6·5 Å. for two layers each consisting of 6 carbonate groups with the aluminium of the $Al_2(CO_3)_3$ accommodated interstitially. However, in the absence of sufficient intensity data for the $00l$ reflections, this model must remain purely hypothetical.

In conclusion, the X-ray data for hydro- and metascarbroites were not considered sufficiently detailed and precise for structural investigations of these phases. Nevertheless, the most prominent differences between their X-ray powder patterns and that of scarbroite appear to be associated with a change in the *c*-parameter of the scarbroite cell.

Acknowledgements.—The authors wish to acknowledge the help of Dr. R. A. Chalmers of the Department of Chemistry, University of Aberdeen, who carried out the chemical analysis; of Dr. C. Daglish of Reckitt and Colman research laboratories, Hull, who provided the infra-red absorption curves; and above all, of Dr. G. W. Brindley who has given such valuable quantitative help.

References.

American Petroleum Institute Research Project 49. Reference Clay Minerals (Columbia University, New York, 1951).

Brindley (G. W.) and Comer (J. J.), 1960. Min. Mag., vol. 32, p. 363.

Duffin (W. J.) and Goodyear (J.), 1957. Nature, vol. 180, p. 977.

Megaw (H. D.), 1934. Zeits. Krist., vol. 87, p. 185.

Melmore (Sidney), 1930. Ann. Rept. Yorkshire Phil. Soc., 1930 (for 1929), Proc., p. 9 [M.A. **4**–479].

Vernon, (W. V.), 1829. Phil. Mag., ser. 2, vol. 5, p. 178.

Electron-optical data for crystals of scarbroite.[1]

By G. W. Brindley, M.Sc., Ph.D., and J. J. Comer, M.S.
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[Read 28 January 1960.]

Summary. Electron micrographs of scarbroite show thin platy crystals of about 1 μ size, having rhombic outlines with angles $66^\circ \pm 1^\circ$ and $113^\circ \pm 1^\circ$. Single-crystal electron-diffraction patterns show rectangular net patterns, with $d_{100} = 9{\cdot}90$ Å., $d_{010} = 14{\cdot}67$ Å., $\gamma^* = 90^\circ - 0{\cdot}05^\circ$. Strong $hk0$ reflections show a pseudohexagonal arrangement, but true symmetry is probably orthorhombic or monoclinic. Faces outlining rhombic forms are of type $\{11l\}$, $\{1\bar{1}l\}$.

A SAMPLE of scarbroite was made available by Drs. Goodyear and Duffin for examination by electron microscope and diffraction methods. With the electron microscope at present available to the writers (R.C.A. model: E.M.U. type 2D, fitted with variable diaphragm for selected area electron diffraction) it was possible to examine fine dispersions of scarbroite and to take single-crystal diffraction patterns for the preferred orientation taken up by the crystals on the stage of the microscope.

Scarbroite is readily dispersed in water and weak suspensions dried on collodion films show clearly the morphology of the individual crystals. Fig. 1 is a typical electron micrograph. The crystals are in the form of thin plates of uniform thickness, with well-defined rhombic outlines, and are about 1 μ in size. The crystals vary in thickness from one to another and a rough estimate of the order of the thickness is 0·01–0·05 μ.

The thinnest crystals have a mottled appearance and the edges sometimes exhibit a rim. The corners of most crystals are not geometrically sharp. These observations suggest that the crystals may be unstable under the conditions existing in the microscope and this would not be surprising in the light of the dehydration data discussed by Goodyear and Duffin in the preceding paper.

The outlines of the crystals are sufficiently sharp and linear to permit the angles between the edges to be measured to within $\pm 1^\circ$. The mean values obtained for eleven crystals are $66^\circ \pm 1^\circ$ and $113^\circ \pm 1^\circ$, the sum

[1] Contribution No. 59–21 from the College of Mineral Industries, The Pennsylvania State University, University Park, Pa.

of which is 179°±2°. These angles are significantly different from 60° and 120° and do not support the tentative hexagonal unit cell suggested by Duffin and Goodyear (1957).

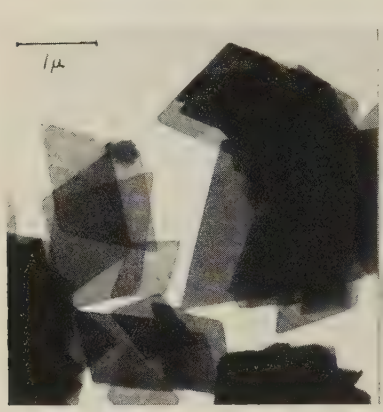

Fig. 1.

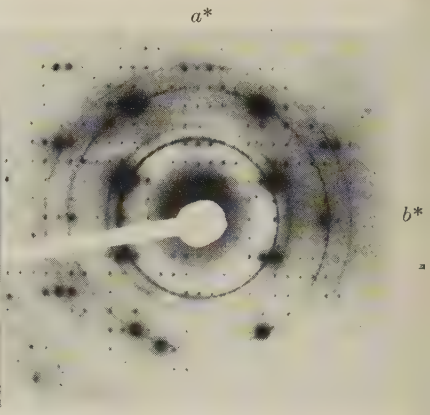

Fig. 2.

Fig. 1. Electron micrograph of scarbroite.
Fig. 2. Single crystal, electron diffraction pattern of scarbroite, with a superimposed ring pattern of aluminium for calibration.

Using thin dispersions, single crystals could readily be selected in the field of the microscope for single-crystal diffraction study. A spot pattern of the type shown in fig. 2 is easily obtained from the thinnest platelets. The pattern shows a rectangular array suggesting an orthorhombic or monoclinic unit cell. The diffraction patterns, when calibrated with respect to MgO and NaCl powder patterns (ring diagrams) taken independently but with identical instrument adjustments, gave parameter variations as large as 1–2 %. More consistent results were obtained by 'shadowing' the scarbroite lightly with aluminium, so that a combined spot pattern with superimposed Al calibration was obtained (see fig. 2). Ring diameters were found to vary by as much as 1–2 % in a single pattern, presumably due to some instrumental defects. Calibrations were made parallel to the principal axes of the rectangular spot patterns and results were then obtained for d_{100} and d_{010} that appear to be reliable to about 0·3 %. The more widely spaced and the less widely spaced point rows were labelled respectively the a^* and b^* axes and the following results were obtained: d_{100} 9·90±0·02 Å., d_{010} 14·67±0·04 Å., d_{010}/d_{100} 1·482±0·007, γ^* 90°±0·5°.

The pseudo-hexagonal character of the strongest reflections is readily

seen in fig. 2, and it is apparent why Duffin and Goodyear came to select an hexagonal cell from X-ray powder data.

The crystal morphology and the diffraction data can be correlated as follows: The diffraction patterns suggest that the c-axis, [001], lies parallel or nearly parallel to the electron beam. It follows that planes of type (hk·0) also have this orientation, and hence the observed angle between the edges of the plates, as seen in the micrographs, will be equal to some interfacial angle $(h_1k_1 0):(h_2k_2 0)$ even if the bounding facets are in fact (hkl) planes and oblique to the c-axis. And since

$$(100):(010) = 90°,$$

$$(100):(1\bar{1}0) = (100):(110) = \tan^{-1}(d_{100}/d_{010}) = 34{\cdot}0°,$$

making $(110):(1\bar{1}0)$ 68·0°, close to the measured value of $66° \pm 1°$. We conclude that the plates are bounded by faces of the forms $\{11l\}$, $\{1\bar{1}l\}$, where l may be zero.

References.

Duffin (W. J.) and Goodyear (J.), 1957. Nature, vol. 180, p. 977.
—— —— 1960. Min. Mag., vol. 32, p. 353.

The Lewisian pegmatites of South Harris, Outer Hebrides.

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Summary. A number of representative examples of the Lewisian acid pegmatites of South Harris are described, and the presence of the following minerals has been established: quartz, albite, microcline, biotite, muscovite, magnetite, beryl, spessartine, gahnite, columbite, monazite, zircon, pyrite, epidote, tourmaline, apatite, thorite, uraninite, thorogummite, uranophane, kasolite, betafite (?), and allanite. Spectrographic, optical, and X-ray powder data are given for some of these minerals, together with chemical analyses of magnetite, biotite, columbite, gahnite, and spessartine. It is believed that gahnite, uranophane, and the pyrochlore mineral (probably betafite) are recorded for the first time from Britain.

As early as 1901 Heddle described a number of minerals from the 'graphic granites' or pegmatites of South Harris at Chiapaval and Roneval. From Chiapaval green muscovite, biotite (haughtonite), microcline, blue quartz, garnet, and beryl were noted, and analyses of the micas given. From the Roneval sheets oligoclase, microcline, magnetite, and biotite were mentioned, with analyses of the last two minerals. Magnetite and microcline were noted from the pegmatites around Stromay.

Later, in 1927, Jehu and Craig remarked on the abundance of these acid pegmatites, especially towards the margin of the granite-gneiss in the Loch Langavat valley (1927, pp. 481–483). A general description was given: 'The felspar is usually microcline, sometimes orthoclase enclosing in perthitic fashion a plagioclase near albite. The perthitic structure is often visible in hand specimen, but also occurs on a microscopic scale. The only other common constituent is a dark mica, in rather small and irregular plates, and another constituent, though less common than the mica, is magnetite in irregular masses an inch or more in length.'

Davidson (1942, pp. 108–109) quoted analyses of the potash feldspars from Chiapaval and Sletteval and an analysis of the latter pegmatite. Robertson (1945) described the Chiapaval and Sletteval sheets, mainly

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in connexion with the extraction of potash feldspars, and recorded the presence of topaz in the Chiapaval pegmatite.

Recently these pegmatites have been mapped in more detail (Dearnley, 1959). In the Loch Langavat belt the pegmatites form concordant pods within the paragneisses, but to the south-west cross-cutting sheets are common, as noted by Kursten (1957, p. 21). In the field two main groups of pegmatites may be recognized: pegmatites with magnetite and biotite and only minor muscovite, and pegmatites with muscovite and only minor biotite and magnetite. Transitional types occur and locally pegmatites almost free from magnetite and micas may be found. Pegmatites of the first group are more common in the Loch Langavat valley (one notable exception occurs to the north-west of Scara Ruadh), and include the large sheets of Sletteval, Roneval, and Beinn Tharsuinn. Pegmatites of the second group occur in the Obbe to Northton paragneiss belt and include the Chiapaval sheet.

Mineralogy.

During the examination of these pegmatites a number of interesting minerals have been found (von Knorring and Dearnley, 1959, pp. 255–256) and it is the purpose of this paper to describe these occurrences. Three pegmatites have been studied in some detail, at Loch a' Sgurr, near Finsbay, at Sletteval, and at Chiapaval. The Sletteval and Chiapaval sheets are thick cross-cutting pegmatites, the former a first group and the latter a second group pegmatite of the present classification. The Loch a' Sgurr pegmatite is a concordant first group variety.

Loch a' Sgurr pegmatite. This pod-like pegmatite is a magnetite–biotite-bearing variety typical of numerous lenses throughout the Loch Langavat valley. Good exposures across the core of the lens have been made by road blasting and the sheared contacts with the surrounding paragneisses are quite clear. The bulk of the pegmatite consists of pink and white albitic plagioclase, some microcline, and quartz. Magnetite segregations up to 6 inches in length are common and are frequently associated with a greenish-yellow mica. Locally the feldspar is a brick-red colour near to the magnetite lenses and in these cases a distinct radioactive anomaly can be detected due to uraninite, thorite, and monazite. Yellow powdery coatings of uranophane on fracture surfaces are common. A list of the minerals identified in the pegmatite comprises: quartz, albite, microcline, biotite, magnetite, epidote, zircon, spessartine, pyrite, allanite, uraninite, thorite, monazite, and uranophane.

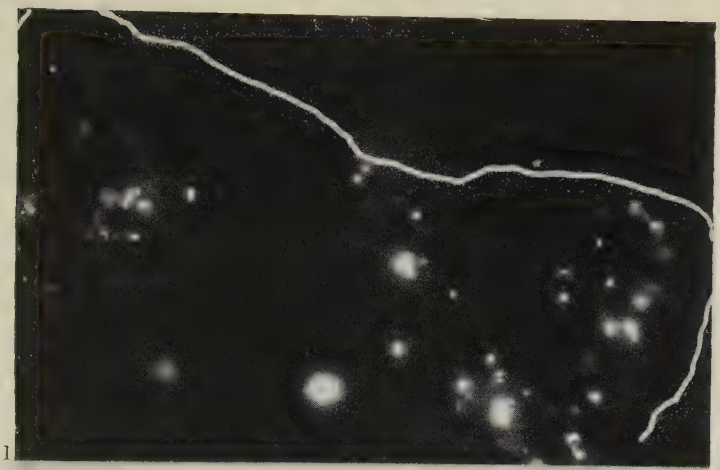
Magnetite is common and often forms streaky lenses within the pegmatite. A partial analysis (table I) indicates only a minor content of TiO_2, and may be compared with a magnetite analysed by Heddle (1901, p. 97), from the 'great granite vein on the east of Roneval' (? Sletteval pegmatite). Epidote occurs as scattered light green crystals, and also intergrown with the albitic plagioclase. Zircon is common and forms euhedral opaline-grey to dark brown slender crystals, showing the prism {100} combined with the pyramid {111}. Frequently a zonal growth is apparent. The zircon is metamict and contains inclusions of magnetite. It is at times overgrown with minute grains of uraninite.

Table I. Chemical composition of magnetite from the Loch a' Sgurr pegmatite.

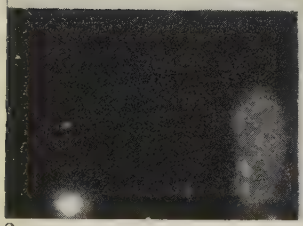
	1.	2.
TiO_2	0·90	—
Fe_2O_3...	67·20	68·10
FeO	27·80	29·10
MnO	0·13	0·50
Al_2O_3...	—	0·62
CaO	—	0·17
MgO	—	0·60
SiO_2	—	1·00
Insol....	1·10	—
	97·13	100·09

1. Magnetite, Loch a' Sgurr pegmatite. Partial anal. O. von Knorring.
2. Magnetite, granite vein east of Roneval. Heddle, 1901, p. 97.

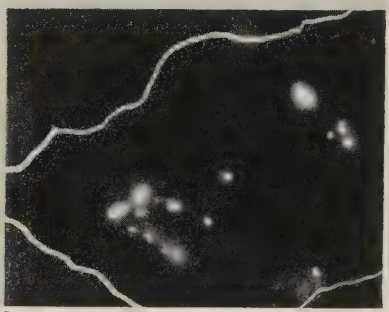
An autoradiograph (fig. 1) indicates that the zircon is sometimes slightly radioactive and in some crystals minute uraninite inclusions are seen. Spessartine garnet is a minor constituent and has a refractive index ($1{\cdot}800 \pm 0{\cdot}003$) close to the analysed spessartine from Chiapaval (table V). Pyrite is locally common. Allanite occurs as small, black, glassy metamict crystals. Uraninite is present in small amounts, sometimes as inclusions in magnetite or monazite, sometimes within feldspar crystals. It may be either black or a dark greenish colour. An autoradiograph (fig. 1) shows well-defined bright spots due to uraninite crystals included in magnetite, and fig. 2 shows similar uraninite grains in monazite. Thorite occurs in a brown glassy metamict state and only gives an X-ray diffraction pattern after heating. Monazite is quite common, often as inclusions in the magnetite but also within the feldspar. It is brownish-red in colour, often showing good crystal faces and occurring in crystals up to $\frac{1}{4}$ inch in length. The optic axial angle is small (+) and the refractive index $\gamma = 1{\cdot}842 \pm 0{\cdot}003$. An autoradio-



1



2



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FIGS. 1–3. Autoradiographs. FIG. 1 (*top*): Loch a' Sgurr pegmatite. ×2. Exposure 14 hours. Bright spots are uraninite, the more diffuse areas are monazite and zircon. Note the uranophane coatings along fractures. FIG. 2 (*bottom left*): Loch a' Sgurr pegmatite. ×2. Exposure 24 hours. Monazite crystal approximately parallel to {010} shows as a diffuse image with bright uraninite inclusions. FIG. 3 (*bottom right*): Sletteval pegmatite. ×2. Exposure 14 hours. Thorite and thorogummite inclusions in biotite crystals.

graph (fig. 2) shows a section of a monazite crystal approximately parallel to {010}, giving a diffuse radiation picture and containing small uraninite inclusions. The radioactivity is probably mainly due to the thorium content, as in the case of the Chiapaval monazite (table II). Uranophane occurs as yellow powdery films on fracture surfaces. It

TABLE II. Qualitative spectrographic analyses of South Harris Lewisian pegmatite minerals.*

Mineral and locality.	Major elements.	Minor elements.	Trace elements.
Loch a' Sgurr			
Zircon	Zr, Si	—	Ca, Hf, Y, Yb, Sc, Fe, Al, Pb, Mg, Ti, Mn
Uraninite	U	—	Si, Pb, Y, Fe, Ca, Mg, Mn, Zr, Al
Sletteval			
Biotite	Al, Si, Fe	K, Ti, Mg, Mn	Ca, Li, Na, Rb, Zn, Co, V, Ga
Microcline	Si	K, Na, Al	Rb, Ca, Fe, Li, Mg, Pb, Mn
Thorite	Th, Si	Ca, U	Y, Pb, Al, Mn, Fe, Mg, Ti
Chiapaval			
Muscovite	Al, Si	K, Fe	Li, Na, Rb, Mg, Mn, Ga, Ti, Ca, Be, Zn, Nb
Microcline	Si	K, Al, Na	Rb, Fe, Ga, Pb, Ca, Mg
Black quartz ...	Si	—	Ca, Mg, Al, Fe, Mn, Pb, Ti
Columbite	Nb	Ta, Mn, Fe	Ba, Ti, Ca, Si, Zr, Mg
Columbite	Nb	Ta, Mn, Fe	Ba, Ti, Ca, Si, Zr, Mg, Al, Pb
Monazite	Ce, Th, P	Nb	Ba, Ti, Ca, Si, Zr, Mg, Al, Pb,Fe, Mn, Y, La, Nd
Zircon	Zr, Si	Hf	Ca, Fe, Al, Mg, Mn, Pb, Th, Y, Nb
Gahnite	Zn, Al, Fe	Mn, Si, K	Li, Na, Rb, Ca, Ba, Cu, Mg, Ga, Ti, Cr
Kasolite	Pb	Th, U, Si	Fe, Mg, Mn, Ca, Ba, Al, Zr, Nb, Y
Kasolite-like mineral	Th, Si	Pb, U	Fe, Mg, Mn, Ca, Ba, Al, Bi, Zr, Nb, Y
Betafite (?) ...	Nb, Ca	Fe, Mn	Y, Pb, Mg, Si, Ti, Zr

* Analysts: Misses J. M. Rooke and A. M. Swallow.

forms minute needle-like crystals in radial groups and aggregates. The refractive index $\gamma = 1{\cdot}699 \pm 0{\cdot}003$, the optic axial angle is small (−), and the elongation positive ($\gamma = c$); the interference colours are abnormal blues of the first order. The X-ray diffraction pattern shows excellent agreement in spacings and intensities with uranophane from the Ruggles pegmatite (Frondel *et al.*, 1956). On the autoradiograph (fig. 1) the thin faint lines are due to uranophane coatings along fractures. It is believed that this uranophane occurrence is the first to be reported from the British Isles.

Sletteval pegmatite. On the Sletteval ridge two large parallel sheet-like pegmatites occur, the lower of which has been quarried for potash feldspar. The country rocks are garnet-metagabbros and metadiorites of the South Harris igneous complex (Dearnley, 1959).

Albite, potash-feldspar, and biotite books make up the bulk of the pegmatite, but scattered magnetite crystals are quite common. Apatite

crystals up to 2 inches in length occur sporadically and small spessartine and zircon crystals have been found in heavy mineral separations. Allanite occurs locally in small amounts, and one example of a flattened elongated crystal 2 inches in length has been found.

Thorite and thorogummite are found as small inclusions in many of the biotite crystals; they range in size from about $\frac{1}{10}$ inch to $\frac{1}{4}$ inch across, but are not common. The thorogummite occurs as glassy red or as earthy red-brown grains, the latter sometimes forming an outer rim or completely replacing the former, and sometimes seen as replacements of the thorite crystals. The red and the brown crystals are not metamict since they give a thorogummite X-ray diffraction pattern without heating, but the pattern is much clearer after heating to 950° C. for 1 hour. The refractive index of these isotropic grains is $1{\cdot}610 \pm 0{\cdot}003$, which indicates that they are thorogummite rather than thorite. Yellow thorite crystals are closely associated with the thorogummites. These are quite metamict and isotropic with a refractive index of $1{\cdot}685 \pm 0{\cdot}003$ and a density of 4·30 before heating. When the crystals are heated to 950° C. for 1 hour the X-ray diffraction pattern indicates that thorianite is the major constituent, but weak lines of thorite are also present. When the heating is carried out at 1400° C. for 17 hours the mineral changes to the monoclinic dimorph of thorite, huttonite, see fig. 4. These results are in accord with the work of Frondel (1953, p. 1015) who stated that 'Microcrystalline thorogummite and metamict thorite react differently when heated to 1000°. The former develops the tetragonal, the latter the monoclinic polymorph of $ThSiO_4$. ThO_2 also is formed in both cases.'

In the Sletteval thorites examined, the weight loss on heating to 1400° C. was 22·6 %, and the final refractive index and density were respectively 1·750 and 4·80.

A qualitative spectrographic analysis of the yellow thorite is given in table II, from which it is seen that the mineral is a uranium-bearing variety. An autoradiograph (fig. 3) shows high radioactivity associated with each thorite or thorogummite grain in the biotite.

The biotite from Sletteval often occurs in fairly large books, some of which are narrow and elongated, apparently along fracture surfaces. In addition to thorite and thorogummite, inclusions of small white crystals of apatite often occur within the biotite books. An analysis is given in table IV and is very close to that of a similar pegmatitic biotite from Mansjö, Sweden (Eckermann, 1925). The analysis also compares favourably with the average composition of granitic and pegmatitic

TABLE III. X-ray powder data (Cu-$K\alpha$ radiation) for betafite from the South Harris pegmatites.

	1.		2.			1.		2.	
hkl.	*d*, Å.	*I.*	*d*, Å.	*I.*	*hkl.*	*d*, Å.	*I.*	*d*, Å.	*I.*
	—		3·99	3		—		1·63	1
	—		3·55	1		—		1·59	1
	—		3·28	1	266	1·55	s	1·55	6
	—		3·19	2	444	1·48	w	1·485	1
222	2·97	vs	2·98	10		—		1·355	1
004	2·58	m	2·57	2	008	1·29	w	1·290	1
	—		2·49	3	266	1·18	w	1·181	2
	—		2·20	1	048	1·15	m	1·154	3
	—		2·00	1	448	1·05	w	1·050	1
044	1·82	s	1·82	8		—		1·025	1
			1·70	2	666	0·99	m	0·990	2

1. Betafite, Chiapaval pegmatite, South Harris.
2. Betafite, Madagascar, Frondel *et al.*, 1956, p. 101.

TABLE IV. Chemical analyses of biotite from the Sletteval pegmatite and of columbite from the Chiapaval pegmatite. Analyst, O. von Knorring.

	1.	1a.				2.	2′.	2a.		
SiO_2	35·75	Si	5·45	$z = 8·00$	SiO_2	1·25	—			
Al_2O_3	17·10	Al	2·55		Al_2O_3					
			0·52		ZrO_2	0·10	—			
TiO_2	2·94	Ti	0·34		FeO	12·41	12·57	Fe·· 2·45	3·80	
Fe_2O_3	3·59	Fe···	0·41		MnO	6·69	6·78	Mn 1·35		
FeO	18·84	Fe··	2·40	$Y = 5·64$	Nb_2O_5	65·20	66·06	Nb 7·00	8·14	
MnO	0·67	Mn	0·09		Ta_2O_5	12·56	12·73	Ta 0·82		
MgO	8·14	Mg	1·85		TiO_2	1·84	1·86	Ti 0·32		
Li_2O	0·05	Li	0·03			100·05	100·00			
CaO	0·04	Ca	0·01							
Na_2O	0·08	Na	0·02	$X = 1·81$						
K_2O	9·17	K	1·78							
H_2O^+	3·72	OH	3·78	3·87						
H_2O^-	0·04	F	0·09							
P_2O_5	nt. fd.									
F	0·18									
Cl	nt. fd.				Sp. gr.	3·03				
S	n.d.				$\beta \approx \gamma$	1·635				
	100·31									
O = F	0·08									
	100·23									

1. Biotite from the Sletteval pegmatite, South Harris.
1a. Atomic ratios of biotite to 24(O, OH, F).
2. Columbite from the Chiapaval pegmatite, South Harris.
2′. Anal. 2 recalculated to 100 % omitting SiO_2, Al_2O_3, and ZrO_2.
2a. Atomic ratios of columbite to 24 oxygen atoms.

biotites as given by Rankama and Sahama (1949, p. 156). Individually, however, pegmatitic biotites differ considerably in chemical composition. The major variations appear to be in the iron, magnesia, water, and fluorine contents. The titania is generally around three per cent. except in the extreme iron-rich varieties, where both magnesia and titania are low.

Trace elements detected in the Sletteval biotite are: Rb, Zn, Co, V, and Ga. It is a relatively iron-rich type with refractive index of $\beta \approx \gamma = 1{\cdot}635 \pm 0{\cdot}003$, and a specific gravity of 3·03.

The Sletteval pegmatite is the only one examined that shows signs of zoning. From the contact inwards a zone of graphic granite is followed by a zone rich in microcline and biotite. Irregular masses of white and bluish quartz are common towards the core.

Chiapaval pegmatite. This large pegmatite sheet, $1\frac{1}{2}$ miles north-west of Northton, runs from Faodail an Taobh Thuath to just north-west of Rudh' an Teampuill, in a north-east to south-west direction. It dips north-west into the slope of Chiapaval and in places is up to 80 feet thick. The pegmatite has been opened up at the north-western end and quarried for potash feldspar. The following mineral assemblage was recorded from the quarried portion of the sheet: quartz, albite, microcline, muscovite, biotite, magnetite, beryl, columbite, gahnite, spessartine, uraninite, thorite, kasolite, a kasolite-like mineral, a betafite-like mineral, zircon, monazite, allanite, blue and black tourmaline, and pyrite. The bulk of the pegmatite consists of quartz and feldspar with muscovite and minor biotite and magnetite. A partial analysis of the muscovite indicated the presence of 4·60 % iron oxide, calculated as Fe_2O_3. The other minerals are present in only small amounts in the pegmatite as a whole but are locally abundant.

Columbite usually occurs as small crystals although specimens up to $1\frac{1}{2}$ inches in length have been found. They are frequently associated with quartz, feldspar, spessartine, and gahnite and locally with muscovite, monazite, and uraninite. Well-formed individual crystals are not common. The specific gravity for a number of separate grains ranges from 5·50 to 5·70, which places them in the columbite range of the tantalite–columbite series. A determination of the specific gravity of the analysed material, by the Berman balance, indicated a value of 5·61, which compares with the calculated specific gravity, from the formula sp. gr. $= (5{\cdot}20 + 0{\cdot}03 \times Ta_2O_5\ \%)$, of 5·58. An analysis of one crystal is given in table IV. On the basis of the ionic radii Ti has been placed in the Nb and Ta group, rather than with Fe and Mn. The ratio

$(FeO+MnO):(Nb_2O_5+Ta_2O_5+TiO_2)$ shows a slight departure from the theoretical ratio of 4:8. The calculated unit cell dimensions from the best lines on the powder diffraction pattern gave the following values: *a* 5·11 Å., *b* 14·21 Å., *c* 5·75 Å., which are close to those recorded previously for the columbite–tantalite series (Sturdivant, 1930, p. 89). Qualitative spectrographic analyses for two columbite crystals are recorded in table II.

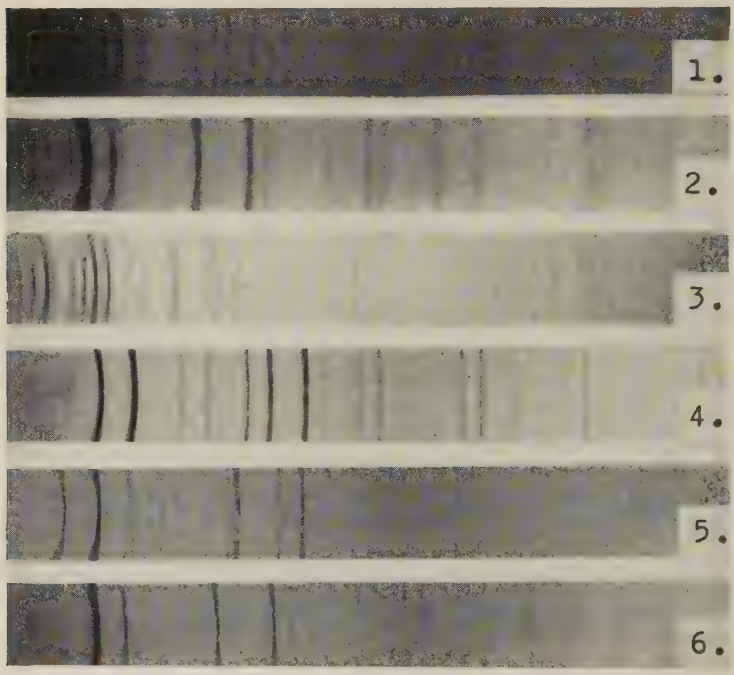

FIG. 4. X-ray powder diffraction photographs. 9 cm. camera, Cu-$K\alpha$ radiation. 1: Uranophane, Loch a' Sgurr pegmatite. 2: Thorite heated to 950° C. for 1 hour. Thorianite is the main constituent. Sletteval pegmatite. 3: Thorite heated to 1400 C. for 17 hours. Huttonite is the main constituent. Sletteval pegmatite. 4: Gahnite, Chiapaval pegmatite. 5: Columbite, Chiapaval pegmatite. 6: Betafite (?), Chiapaval pegmatite.

The zinc spinel, gahnite, occurs sporadically, sometimes in relatively large crystals, but also in irregular masses often associated with muscovite. The specific gravity, as determined on the Berman balance, is 4·55, the refractive index is $1·795 \pm 0·003$, and the calculated unit-cell dimension is 8·10 Å. for the analysed specimen in table V. The analysis

compares closely with a pegmatitic gahnite from the Rosendal pegmatite, Kimito, Finland (Pehrman, 1948, p. 330). Kullerud (1953) has determined the temperature of formation of the Rosendal blende (von Knorring, 1946) as approximately 535° C. It is interesting to note that in the Rosendal occurrence the coexisting blende and gahnite have similar zinc:iron ratios, in the blende 5·6 and in the gahnite 5·4, suggesting that the iron content in gahnites may also be a function of the temperature of formation. In the analysis of the Chiapaval gahnite the ratios do not exactly correspond to the theoretical ratios, and this probably indicates the presence of some 1·4 % Fe_2O_3 in the total iron percentage. Trace elements detected in the analysed gahnite are: K, Li, Na, Rb, Ca, Ba, Cu, Be, Ga, Ti, and Cr. In the Kimito gahnite Pehrman (1948) records the presence of Li, Cd, Be, In, and Ga.

TABLE V. Chemical composition of gahnite, spessartine, and an oligoclase zoisite intergrowth from South Harris.

	1.	2.	3.	1a.		2a.
SiO_2	0·12	36·10	57·71	Al ... 15·91		Si ... 23·6
TiO_2	nt. fd.	n.d.	—	Zn ... 6·40		Al ... 16·1
Al_2O_3... ...	55·91	20·87	25·09	Fe ... 1·60	8·13	Fe··· ... 2·0
Fe_2O_3... ...	n.d.	4·10	0·29	Mn... 0·09		Fe·· ... 8·9
FeO	7·90	16·20	0·04	Mg... 0·04		Mn ... 11·9
ZnO	35·85	—	—			Mg ... 0·5
MnO	0·42	21·47	0·04			Ca ... 0·4
MgO	0·12	0·57	n.d.			
CaO	tr.	0·51	8·12			
Na_2O... ...	—	—	7·33			
K_2O	—	—	0·74			
H_2O+ ...	—	—	0·84			
H_2O- ...	—	—	0·12			
P_2O_5	—	—	tr.			
	100·32	99·82	100·32			

1. Gahnite from the Chiapaval pegmatite. Total iron taken as FeO. Anal. O. von Knorring.

1a. Gahnite, atomic ratios to 32 oxygen atoms.

2. Spessartine from the Chiapaval pegmatite. Anal. O. von Knorring.

2a. Spessartine, atomic ratios to 96 oxygen atoms.

3. Oligoclase–zoisite intergrowth, Loch Vallarip. Anal. J. R. Baldwin.

Spessartine garnet is a fairly common constituent of the pegmatite and is locally abundant, forming irregular masses up to 6 inches across. The refractive index is 1·805±0·003, and the specific gravity 4·19. A calculation of the unit cell dimension from the powder diffraction pattern gave a value of 11·60 Å. From the analysis (table V) the ratios $RO:R_2O_3:SiO_2 = 2·61:1:2·49$. If all the iron is calculated as FeO,

however, the ratios become 2·94:1:2·97, and on this basis the constituent molecules of the garnet may be calculated as spessartine 54·5 %, almandine 41·2 %, pyrope 2·7 %, and grossular 1·6 %.

Allanite and zircon are present in the pegmatite in small amounts. The allanite is always metamict. Zircon is commonly associated with the radioactive mineral assemblages; it is brownish pink in colour and forms curved intergrown crystal aggregates, the type known as cyrtolite. The minor hafnium content of the zircon is notable. Rankama and Sahama (1950, p. 568) have indicated that 'the minerals with a high Hf:Zr ratio are more strongly radioactive than are the zircons and zirconium silicates with a lower content of hafnium'. This is consistent with the presence of thorium in the Chiapaval zircon (table II) and its association with uraninite and thorite.

Uraninite occurs in the pegmatite but is not common. Frequently it is closely associated with the columbite and often forms small inclusions within the latter. The specific gravity determined by Berman balance on one such inclusion was 10·28 and from the powder diffraction pattern of this individual the unit cell dimension has been calculated as 5·45 Å.

Kasolite, thorite, and monazite are sparingly distributed throughout the pegmatite, but two or more minerals may be in close association, often in small aggregates with spessartine, columbite, and zircon. Thorite and a pyrochlore mineral, probably betafite, are metamict and give X-ray powder patterns only after heating. A qualitative spectrographic analysis of the betafite is given in table II, and the X-ray powder data in table III, from which the unit cell dimension has been calculated as 10·30 Å. Kasolite, a hydrated uranium–lead silicate, is associated with uraninite and columbite, and a kasolite-like mineral, predominantly a thorium–lead silicate but with an X-ray diffraction pattern similar to kasolite, is seen surrounding uraninite as an olive-green rim.

Loch Vallarip pegmatite. Small pegmatitic veins composed essentially of a very distinctive pink feldspar are found just west of Loch Vallarip in the Rodilpark area of South Harris, cutting garnet-metagabbros of the igneous complex. In thin section the feldspar is seen to consist of large crystals of well-twinned oligoclase (An_{25}). A considerable amount of zoisite occurs in parallel arrangement with the feldspars or sometimes irregularly arranged and coalescing into larger aggregates. All the feldspar is crowded with minute flecks of sericite and scapolite, and locally slightly larger plates of scapolite, muscovite, and quartz occur. A few small allanite grains with epidote rims are present, but the total amount of these inclusions in the feldspar is small. An analysis of

the feldspar is given in table V from which the composition may be calculated in terms of a single feldspar phase of composition $Or_{4\cdot5}Ab_{67\cdot0}An_{28\cdot5}$, or approximately as oligoclase 82·0 % and zoisite 15·0 %. A modal analysis indicates the proportions oligoclase 80 %, zoisite 16 %, other minerals 4 %. Owing to the extreme difficulty of measuring such an intimate intergrowth these figures can only be an approximation, but they compare well with the recalculated analysis.

A qualitative spectrographic analysis of the intergrowth indicated the presence of the following elements in trace amounts: Rb, Sr, Ba, Be, Ga, Cu, Mg, Ti, Pb, V, Cr, Mn, and Fe.

The calculated composition of the original feldspar phase before replacement by the oligoclase–zoisite intergrowth is very close to the feldspar from an intermediate pegmatite from the Port Eisgein area (Dearnley, 1959, p. 227) which has a composition $Or_{5\cdot5}Ab_{61\cdot2}An_{33\cdot3}$. This pegmatite belongs to the late stage minor intrusives of the igneous complex and not to the subsequently intruded acid-pegmatites associated with the granitic injection complex. It is possible that exsolution in the Loch Vallarip feldspar was produced by retrograde metamorphism and access of water during the intrusion of the acid injection complex.

General observations.

Most of the pegmatites in South Harris are believed to be genetically connected with the granitic injection complex of the area. On the basis of their rare-element content they are closely related, although their bulk compositions may vary considerably. It is thought that the original pegmatitic material consisted of granitic solutions and that after emplacement only a limited exchange of material has taken place. Rearrangement of elements has occurred at various stages during metamorphism. At the south-eastern end of the Loch Langavat valley in particular, a number of pegmatites have been affected by retrograde metamorphism with the subsequent formation of epidote, possibly induced by the dynamic effects associated with the Outer Isles Thrust Plane. A significant feature from the mineralogical point of view is the striking development of magnetite in the biotite-bearing pegmatites, which appears to be connected with a partial disappearance of biotite. Another peculiarity of all the pegmatites in South Harris is the scarcity of tourmaline. Although a substantial number of rare-element minerals have been observed, they are of sporadic occurrence and their distribution is limited. Compared with other areas there is a close resemblance with numerous pegmatites from the Iveland and Evje districts in South

Norway (Barth, 1947) and with pegmatites from the Bancroft area of Ontario, Canada (Satterly, 1957).

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References.

Barth (T. F. W.), 1947. Norges Geol. Undersök., no. 168, p. 5.

Davidson (C. F.), 1942. Trans. Roy. Soc. Edinburgh, vol. 61, p. 71.

Dearnley (R.), 1959. Metamorphic petrology and history of the Lewisian rocks of South Harris, Outer Hebrides. Ph.D. thesis, University of Leeds.

Eckermann (H. von), 1925. Tschermaks Min. Petr. Mitt., vol. 38, p. 277.

Frondel (C.), 1953. Amer. Min., vol. 38, p. 1007.

—— *et al.*, 1956. U.S. Geol. Surv. Bull. 1036–G, p. 91.

Heddle (M. F.), 1901. The mineralogy of Scotland. Edinburgh. 2 vols.

Jehu (T. J.) and Craig (R. M.), 1927. Trans. Roy. Soc. Edinburgh, vol. 55, p. 457.

Knorring (O. von), 1946. Comp. Rend. Soc. Géol. Finlande, vol. 19, p. 77.

—— and Dearnley (R.), 1959. Nature, vol. 183, p. 255.

Kullerud (G.), 1953. Norsk Geol. Tidsskr., vol. 32, p. 61.

Kursten (M.), 1957. Trans. Edinburgh Geol. Soc., vol. 17, p. 1.

Pehrman (G.), 1948. Bull. Geol. Inst. Upsala, vol. 32, p. 329.

Rankama (K.) and Sahama (Th. G.), 1950. Geochemistry. Chicago, The University of Chicago Press.

Robertson (T.), 1945. Potash Felspar. Geol. Surv. Gt. Brit., Wartime Pamphlet no. 44.

Satterly (J.), 1957. Ontario Dept. Mines, 65th Ann. Rept., p. 1.

Sturdivant (J. H.), 1930. Zeits. Krist., vol. 75, p. 88.

An X-ray study of exsolution phenomena in the Skaergaard pyroxenes.

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Summary. The single crystal X-ray methods for the study of exsolution phenomena in pyroxenes previously described by the authors have been applied to the pyroxenes of the Skaergaard intrusion. The results for about fifty pyroxene crystals, selected from various levels between the chilled margin and a height of 2600 metres in the layered series, are presented and are correlated with previous optical descriptions. Whilst the correlation between the results of the optical and X-ray examinations is in general satisfactory, the present investigation shows that the X-ray techniques can in some cases extend our knowledge of the Skaergaard pyroxenes.

THE fine-scale textures of pyroxenes have nowadays achieved an importance and complexity rivalled only by the feldspars. The more important exsolution lamellae commonly occurring in both clino- and ortho-pyroxenes have been carefully studied under the microscope, particularly during the last 25 years, and the opinions as to their nature and significance as summed up by Poldervaart and Hess (1951) are now widely accepted. To some workers it has seemed that the identification of the lamellae (which can be exceedingly fine) as augite, pigeonite, or ortho-pyroxene on the basis of their orientation, supported by such of their optical properties as can be observed, was not always conclusive; however, it was not until recently that the methods of X-ray diffraction were used to make positive identification of lamellae (Morimoto, 1956; Gay and Bown, 1957). This first X-ray work confirmed that the (001) lamellae in several pigeonites did consist of augite, as had been suggested from the optical data. A routine X-ray method of identification of pyroxene intergrowths of several kinds has been suggested by Bown and Gay (1959), but no detailed correlation of the results of X-ray and optical examination of a suite of pyroxenes has yet been described.

The wide range of compositions and textures of the pyroxenes of the Skaergaard intrusion, originally described by Wager and Deer (1939), makes them particularly suitable for a comparison of the X-ray and microscopic methods, especially as a detailed study of the exsolution textures has recently been published by Brown (1957). In passing it is interesting to note that Wager and Deer (1939, p. 81) suggested that X-ray methods should be used to identify lamellae in their clinopyroxenes, but as far as we know this idea was not pursued until the present study twenty years later. About fifty pyroxene crystals, selected from various levels between the chilled margin and a height of 2600 metres in the layered series, have now been examined by X-ray techniques; the results of this study are presented here. As will be seen, in many cases the results of the optical work are confirmed, but some corrections are necessary and certain important additional information is obtained.

Experimental techniques.

It was found important to select for X-ray study crystals whose exsolution texture could be clearly seen with the microscope, and which corresponded as closely as possible to what could be seen of the same pyroxene in thin section. For this purpose well-shaped (100) or (110) flakes can be used, but (010) flakes are the best since they show clearly the traces of (001) and (100) lamellae; these (010) flakes occur more frequently in crushed pyroxene than is suggested in the literature. This comparison of the optics of the crystal and the thin section is necessary because of the variability of exsolution texture in a single rock, and for the same reason it was the practice to X-ray more than one crystal of each pyroxene. It must be emphasized that in work of this type in the pyroxenes, as in the feldspars, the combination of X-ray and optical studies is more valuable than either alone.

No attempt was made to determine unit cell parameters; the purpose was restricted for the present to the identification of the phases present and their relative orientations. For each crystal, *c*-axis oscillation photographs were taken in two 15° ranges as described in a previous paper (Bown and Gay, 1959). The photographs obtained mostly corresponded to one of the five combinations of pyroxene phases listed there, but two new arrangements were found and will be described.

The diffraction patterns to be expected from inverted pigeonite crystals were not discussed in the previous paper, and must now be considered. According to Poldervaart and Hess (1951) pigeonite on inver-

sion forms an ortho-pyroxene that nearly always retains the *b* and *c* axial directions of the pigeonite. On the other hand Brown (1957) found that the inverted pigeonites of the Skaergaard rocks do not often retain this orientation, but are usually randomly oriented compared

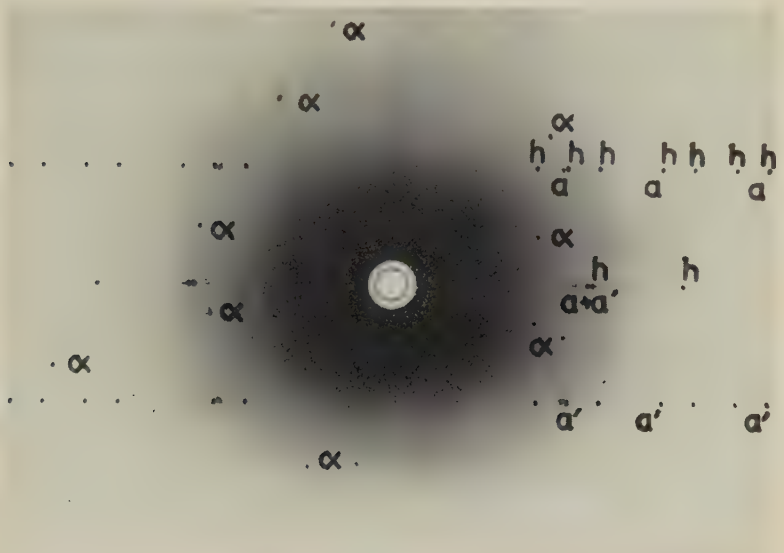

FIG. 1. Central portion of 15 *c*-axis oscillation photograph of inverted pigeonite from 1849 (perpendicular feldspar rock), taken with filtered Fe radiation. The X-ray beam was parallel to the *b*-axis in the centre of the oscillation range. Ortho-pyroxene spots (*h*) and slightly diffuse spots from post-inversion exsolution of augite (*a*, *a'*) are related by the symmetry elements, whereas spots (x) from augite formed before or at inversion are not. (Camera radius 3 cm., photograph enlarged ×1·25 approx.)

with the pigeonite axes. Therefore, in the crystals examined, the augite that exsolved on the (001) plane from the original pigeonite should normally have a random orientation with respect to the ortho-pyroxene. This augite would thus produce apparently randomly occurring diffraction spots, not related by the ortho-pyroxene symmetry elements, on the single-crystal photographs of the inverted pigeonite. Such random spots are characteristic of photographs of Skaergaard inverted pigeonites (fig. 1). The complexity of the powder pattern of augite makes it almost impossible to prove conclusively that these random diffraction spots are produced by augite, but the fact that such spots only occur in strength on photographs of inverted pigeonites makes the explanation

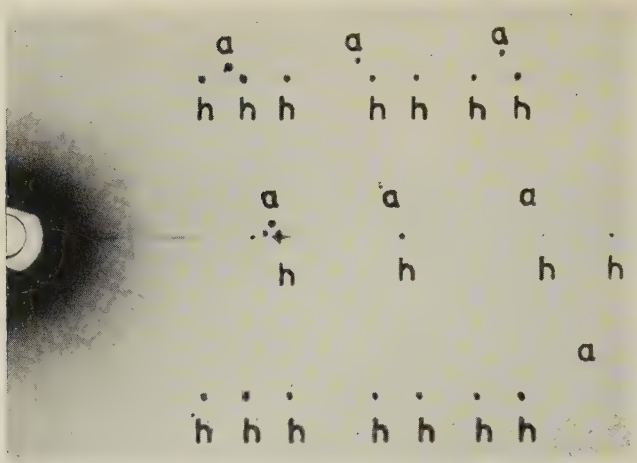

FIG. 2. Part of oscillation photograph of inverted pigeonite from 4087 (0 m.) showing ortho-pyroxene (*h*) and related augite (*a*) spots due to retention of orientation at inversion. Photograph taken under same conditions as fig. 1, but enlargement ×1·75 approx.

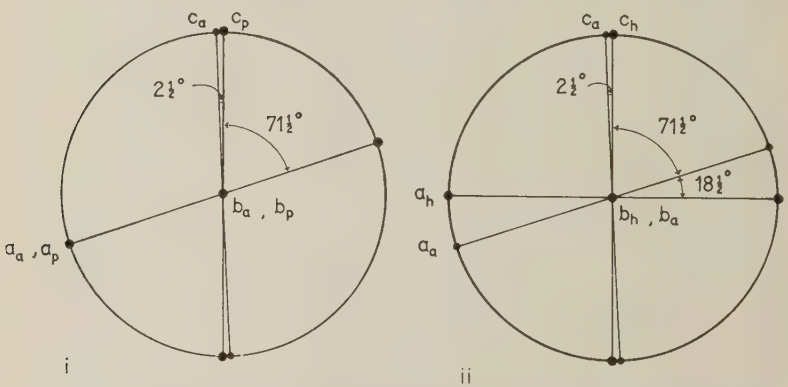

FIG. 3. (i) Orientation of augite and pigeonite axes before inversion of pigeonite. (ii) Orientation of augite and ortho-pyroxene axes after inversion, assuming orientation retained. Subscripts: *a* = augite, *p* = pigeonite, *h* = ortho-pyroxene.

most plausible. Augite exsolved after inversion would, of course, share the (100) plane with the ortho-pyroxene in the normal way, as shown in fig. 1.

Among all the inverted pigeonite crystals examined, only one was found that had retained orientation; its diffraction pattern is reproduced in fig. 2. The corresponding axial orientation is shown in fig. 3,

compared with the orientation before inversion. The scheme is exactly as described by Poldervaart and Hess. Subsequent exsolution of augite would share (100) with the ortho-pyroxene, and so would have a slightly different orientation from the earlier augite.

Presentation of results.

No general account of the Skaergaard intrusion is necessary as the original work of Wager and Deer (1939) is well known, neither is the detailed study of the pyroxene phases and their relation to the crystallization history of the intrusion, which was given by Brown (1957), recapitulated here. Such microscopic description as is relevant will be given in each case; these descriptions have either been taken from Brown (1957) or were contributed personally by Dr. G. M. Brown or Dr. I. D. Muir. The pyroxenes will be considered in order of crystallization, from the chilled margin rocks, through the border group and upwards through the layered series. Only the pyroxene constituents of the crystals will be described although other phases, notably magnetite, ilmenite, and clino-amphibole were often detected by the X-ray method.

The specimen numbers, which should strictly be prefaced by E.G., refer to rocks from the East Greenland geological collection at Oxford.

Chilled margin. The rock examined was 1825, which contains both clino- and ortho-pyroxene. The augite has fine lamellae parallel to (001), and the two crystals examined by X-rays proved that these consisted of pigeonite. One of the crystals showed in addition a trace of ortho-pyroxene, sharing the (100) plane with the augite, though no (100) lamellae could be detected optically.

Texturally the ortho-pyroxene is an inverted pigeonite containing exsolved blebs of augite. Two crystals were examined, both showing strong unsymmetrically placed diffraction spots due to disoriented material. As has been explained above, this is consistent with the formation of ortho-pyroxene by pigeonite inversion with non-retention of the axes. One of the crystals also showed weak oriented augite spots, presumably due to post-inversion exsolution. No sign of (100) lamellae was detected optically.

Gabbro-picrite. In rock 4526 A, the texture indicates that a diopsidic augite crystallized early, while poikilitic plates of ortho-pyroxene formed later from the interprecipitate liquid. No lamellae were observed microscopically in the augite, but all four crystals examined by X-ray diffraction gave spots indicative of two orientations of pigeonite in addition to the augite (fig. 4). In one orientation it seems that the

pigeonite shares the (001) plane with augite as usual, but in the second orientation the *c*-axis of the pigeonite is almost (but conclusively and reproducibly not quite) parallel to that of the augite. This unusual intergrowth is discussed later.

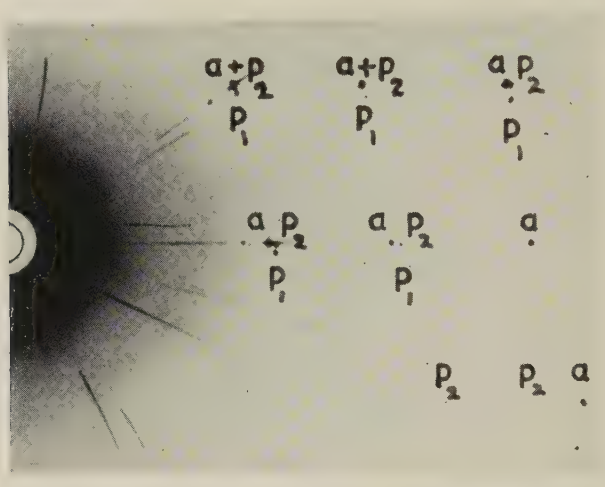

FIG. 4. Part of oscillation photograph of augite from 4526 (gabbro-picrite), showing reflections from the host augite (*a*) together with two orientations of pigeonite (p_1, p_2). Same conditions as fig. 1, enlargement $\times 1{\cdot}75$ approx.

The ortho-pyroxene shows lamellae parallel to (100), identified as augite microscopically; this is confirmed by the X-ray examination of three crystals.

Perpendicular feldspar rock. The rock 1851 described by Brown (1957) differs slightly from 1849, which was used for the X-ray work. For example, the augite of 1849 has many fine and closely-spaced (001) lamellae as well as the broad, widely-spaced (100) lamellae of ortho-pyroxene, whereas in 1851 there are very few of the fine lamellae. The two crystals of 1849 augite chosen for X-ray examination were not representative of the augite texture, for they contain virtually none of the broad lamellae. The photographs show augite and pigeonite sharing the (001) plane, and a small amount of ortho-pyroxene. This is interpreted as showing that the fine (001) lamellae consist of uninverted pigeonite, while the broad (100) lamellae are of ortho-pyroxene.

In contrast to 1851, in which the calcium-poor phase is entirely original ortho-pyroxene, in 1849 there is also some inverted pigeonite, with a blebby texture of augite exsolution. X-ray diffraction from

two of these crystals gave patterns with strong unsymmetrically placed spots, typical of inverted pigeonite in which the axial orientation has not been preserved; slight exsolution of augite after the inversion is also indicated.

Layered series. The augites of the lowest members of the layered series, up to about 30 metres, contain both coarse (100) lamellae and fine (001) lamellae, as in the perpendicular feldspar rock 1849, but with the proportion of (100) lamellae becoming smaller with increasing height.[1] From about 30 metres up to about 1800 metres only (001) lamellae have been reported. The low birefringence of both sets of lamellae together with the fact that the calcium-poor pyroxene in the same rocks is inverted pigeonite led Brown (1957) to conclude that these lamellae are now probably all ortho-pyroxene, though the fine (001) lamellae were originally pigeonite and have inverted on cooling.

About twenty augite crystals from various levels up to 1800 metres were examined. The X-ray photographs of five crystals of 4087 (0 m.) augite showed the presence of both pigeonite and ortho-pyroxene in varying proportions, whereas crystals from 4084 (400 m.), 2307 (850 m.), 1691 (1100 m.), 2573 (1700 m.), and 1907 (1800 m.) all proved to contain pigeonite sharing the (001) plane with the host augite, but no ortho-pyroxene. It is concluded, therefore, that the pigeonite in the (001) lamellae has not inverted in any of these rocks, even when the same crystal has exsolved (100) ortho-pyroxene lamellae below the inversion temperature.

Above about 1800 metres in the layered series no lamellae have been seen in the augites, though in a crystal from 4144 (2300 m.) a little pigeonite was detected by the X-ray method. At about the level of the purple band (2350-2500 m.), the pyroxene occurs as interlocking disoriented grains of a green colour, often crowded with opaque granular inclusions; associated with some of the green pyroxenes, sometimes internal to them and sometimes bordering them, is a brown pyroxene usually in crystallographic continuity with the green. Both the green and brown varieties are ferro-augites, though the green pyroxene appears to have a slightly lower calcium-content and is thought to be inverted from an iron-rich β-wollastonite (Wager and Deer, 1939); no exsolution lamellae have been observed in either variety. X-ray examination of the brown ferro-augites of 4143 (2400 m.) and 1881 (2500 m.) shows only the simple

[1] There is now some evidence to suggest that rocks previously considered as the lowest members of the exposed layered series may in fact be more properly assigned to the border group (Prof. Wager, oral communication).

diffraction patterns of augite with no detectable exsolution; the green pyroxenes of 1974 (2375 m.) and 1881 are also single-phase augites. The green pyroxene of 4143 does show exsolution of an appreciable amount of a pigeonite, whose composition is likely to lie close to clinoferrosilite. The diffraction patterns from this specimen are notable also in that they show a streak joining the spots from the augite and pigeonite components; although this has been recorded for specimens from other localities (Bown and Gay, 1957), this feature of the diffraction patterns is unique to those of the green pyroxene 4143 from among all the rest of the Skaergaard specimens examined. In the specimen 4139 (2600 m.) from the unlaminated layered series that was examined, there is again a green pyroxene mantled by a brown variety. It proved very difficult to obtain single crystals suitable for X-ray study. Photographs from the one crystal of the green pyroxene that was found suggest that there is no exsolution; no suitable specimens could be obtained from the brown variety.

The calcium-poor pyroxene of the layered series is predominantly inverted pigeonite, with complex exsolution textures ranging from poorly developed (100), (010), and (001) plates low in the series to well-developed regular (001) lamellae higher up. These lamellae developed before inversion, and the indices refer to the original pigeonite axes. In all these inverted pigeonites there was post-inversion exsolution of augite parallel to (100) of the ortho-pyroxene. As few of the crystals have retained the pigeonite axes on inversion, in the majority of cases the pre-inversion lamellae are not crystallographically related to the ortho-pyroxene axes and so cannot be usefully investigated by the X-ray method. Most of the crystals examined from 4087 (0 m.), 4084 (400 m.), 4341 (1300 m.), and 4430 (1600 m.) were of this type, giving strong unsymmetrically placed diffraction maxima of augite, together with weak oriented spots indicating the post-inversion lamellae of augite parallel to (100). A description of the axial scheme and diffraction patterns from a crystal of 4087 that has retained orientation on inversion has been discussed in a previous section.

Above 1300 metres a few grains of the pigeonite have resisted inversion, and these show (001) lamellae. X-ray examination of crystals from 4341 (1300 m.), 4430 (1600 m.), 1907 (1800 m.), and 4147 (2050 m.) confirmed that these lamellae are augite. Higher rocks contain no calcium-poor pyroxene as a separate phase. None of the pigeonite, whether host or lamellae, produced the diffuse diffraction spots with $(h+k)$ odd reported for other pigeonites by Bown and Gay (1957).

Discussion.

In general the correlation between the X-ray and optical identification may be considered most reassuring. The present investigation has, however, not merely confirmed but has also extended our knowledge of the Skaergaard pyroxenes in two respects. Firstly, of crystallographic interest rather than petrological, is the discovery that the (001) pigeonite lamellae in augite have not inverted to ortho-pyroxene, even though the same augite crystal may also contain (100) ortho-pyroxene lamellae, and though the associated calcium-poor pyroxene may be inverted pigeonite. The frequent non-retention of axes on inversion, and the presence in some of the rocks of small quantities of uninverted pigeonite may be regarded as evidence that pigeonite crystals experience difficulty in accomplishing the energetically desirable transformation to ortho-pyroxene on cooling. In the arrangement of silicon-oxygen chains pigeonite and augite are likely to be more closely related to one another than are augite and ortho-pyroxene. In the thin pigeonite lamellae it must be presumed that the structurally similar augite tends to stabilize the pigeonite structure, and to increase the general sluggishness of the transition to such a degree that, in the Skaergaard intrusion at least, no transformation has occurred. Whether the transformation has occurred in the augites of other plutonic masses is a matter for speculation and further experiment. Muir (1954) has proposed a similar explanation for the partial retention of pigeonite in a rock from the Beaver Bay diabase.

In addition, the present study has provided several instances of the detection of exsolution by the X-ray method where no lamellae have been described in the thin section work. Many of these are trivial, such as the discovery of pigeonite exsolution in 4144 (2300 m.) or the presence of ortho-pyroxene as well as pigeonite in the augite of 1825 (chilled margin). The appearance of pigeonite in two orientations in the augite of 4526 A (gabbro picrite) is a more remarkable instance, and is of some petrological significance. In the same rock the calcium-poor pyroxene is a bronzite (i.e. not an inverted pigeonite) that crystallized later than the augite from the interprecipitate liquid. As the trend of differentiation is from ortho-pyroxene to pigeonite it is certainly to be expected that any exsolution lamellae in the augite would be ortho-pyroxene. The perpendicular feldspar rock, thought to be of later formation, contains augite with broad ortho-pyroxene lamellae, which give place to pigeonite lamellae in still later rocks at the base of the exposed layered series. It is thus apparently anomalous that pigeonite should exsolve

from the augite of 4526 A. There remains also the problem of interpretation of the two orientations of pigeonite, so that this rock and others of the same horizon merit further investigation.

Conclusions.

The validity of the optical identification of lamellae as set out by Poldervaart and Hess (1951) has been largely confirmed, but the X-ray method has proved itself a valuable complementary tool to thin section work, particularly in the positive identification of very fine lamellae, and in cases where exsolution may be suspected but cannot be observed microscopically.

Acknowledgements. For the opportunity of working on pyroxenes from the Skaergaard intrusion the authors are deeply indebted to Prof. L. R. Wager, F.R.S., and Prof. W. A. Deer; from both Prof. Wager and Prof. C. E. Tilley, F.R.S., they have received much encouragement during the present investigation. They also wish to express their thanks to Dr. G. M. Brown and Dr. I. D. Muir for much helpful advice and many valuable discussions. Mr. K. O. Rickson took many of the X-ray photographs.

References.

Bown (M. G.) and Gay (P.), 1957. Acta Cryst., vol. 10, p. 440.

——, 1959. Amer. Min., vol. 44, p. 592.

Brown (G. M.), 1957. Min. Mag., vol. 31, p. 511.

Morimoto (N.), 1956. Proc. Japan. Acad., vol. 32, p. 750.

Muir (I. D.), 1954. Min. Mag., vol. 30, p. 376.

Poldervaart (A.) and Hess (H. H.), 1951. Journ. Geol., Chicago, vol. 59, p. 472 [M.A. **11**–290].

Wager (L. R.) and Deer (W. A.), 1939. Medd. Grønland, vol. 105, no. 4, p. 1 [M.A. **11**–32].

A note on a nordmarkite and an associated rare-earth mineral from the Ben Loyal syenite complex, Sutherlandshire.

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[Taken as read 5 November 1959.]

Summary. A nordmarkite from the Ben Loyal syenite complex has been analysed, in which a powdery yellow mineral occurs in miarolitic cavities. The mineral may be a new hydrated species with a monazite structure and a chemical composition essentially that of monazite but with silicon partly replacing phosphorus and with magnesium, calcium, and iron partly replacing the rare earths.

A NORDMARKITE from the Lettermore quarry on the shores of Loch Loyal, typical of extensive areas of the Ben Loyal mass from this locality westwards to Sgor Chaonasaide, has been analysed (table I). It is chemically and mineralogically related to the pulaskites described by Read (1931, p. 177) and King (1943, p. 160) from the Cnoc na Cuilean intrusion. A modal analysis indicates the presence of about 12 % of quartz and 9 % of blue-green hornblende. The feldspar consists of albite and a slightly microperthitic orthoclase. Hornblende shows pleochroism α yellow-green, β green, γ blue-green, and the absorption scheme is $\gamma > \beta > \alpha$. A fair amount of sphene occurs, in which a qualitative spectrographic analysis shows minor Al, Fe, Mn, and Mg, and traces of Zr, Y, Ce, V, Pb, Sn, La, Nb, Na, Cr, Ba, Yb, and possibly Eu. The rock shows a holocrystalline texture in thin section, but in the field a faint foliation is often apparent.

Pegmatitic veins in nordmarkite. Heddle (1901) described the mineral association thorite, amazonite, babingtonite, magnetite, topaz, galena, sphene, and rubinglimmer from the cliffs of Sgor Chaonasaide and from an erratic boulder on Beinn Bhreac to the north. This mineral association probably occurs in pegmatitic veins cutting the main nordmarkite in the Sgor Chaonasaide cliffs. Other veins containing the association amazonite, magnetite, sphene, and allanite are present. The amazonite is perthitic in appearance and the green coloration is often patchy and

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irregular. A qualitative spectrographical analysis of the amazonite indicates traces of Fe, Ba, Na, Rb, Ca, Mg, Pb, and Mn.

TABLE I. Chemical compositions of nordmarkite and of the yellow rare-earth mineral.

	1.	2.		1 N.	1 M.
SiO_2	64·94	18·84	Quartz	4·8	12·0
TiO_2	0·81	1·90	Orthoclase	33·8	29·4
Al_2O_3	16·25		Albite	51·4	47·4
$(La,Nd)_2O_3$, CeO_2 ...	—	32·00	Hypersthene ...	0·5	—
			Diopside	5·9	—
Fe_2O_3	1·68	10·61*	Acmite	0·8	—
FeO	1·00	n.d.	Hornblende	—	9·2
MnO	0·06	0·04	Magnetite	0·7	1·0
MgO	1·03	1·90	Ilmenite	1·3	—
CaO	1·56	6·61	Sphene	—	1·0
Na_2O	6·08	—	Apatite	0·5	tr.
K_2O	5·88	—	Hematite	0·3	—
H_2O+	0·38	6·51†		100·0	100·0
H_2O-	0·14	6·06			
P_2O_5	0·26	15·87			
ZrO_2	n.d.	—			
	100·07	100·34			

1. Nordmarkite, Lettermore quarry, Loch Loyal. Anal. O. von Knorring.
2. Yellow mineral from nordmarkite, Lettermore quarry, Loch Loyal. Anal. O. von Knorring.
1 N. Norm of nordmarkite, anal. 1.
1 M. Mode of nordmarkite, anal. 1.

* Total iron as Fe_2O_3. † Loss on ignition.

Yellow mineral in nordmarkite. A striking feature of the nordmarkite from the Lettermore quarry is the abundance of miarolitic cavities often filled with a canary-yellow, kaolin-like mineral. The cavities are up to a few millimetres across and contain, apart from this yellow mineral, aggregates of an albitic plagioclase and apatite, a zeolite mineral, identified as harmotome, forming white pseudo-tetragonal crystals, together with the mineral constituents of the nordmarkite. The yellow mineral is powdery to fluffy in appearance with a specific gravity of about 2·90 and a mean refractive index of $1·647 \pm 0·003$. Both the unheated and the ignited material gave X-ray powder photographs similar to monazite, and no extra lines indicating the presence of admixed impurities were observed. A qualitative spectrographic analysis of a specimen of the yellow mineral shows the presence of the following:

Major elements: La, Fe, Ce, Si, P.
Minor elements: Al, Ca, Mg.
Trace elements: Ba, Sr, Ti, Pb, Mn, Zr, Be, V, Ga, Na.

A tentative chemical analysis, made on 90 mg. of picked material, is given in table I. As the mineral is often intergrown with finely crystalline apatite the figures for calcium and phosphorus may be too high. Due to the small amount of material available for analysis the water content is based on the loss on ignition and halogens like F and Cl have not been determined. The data so far obtained indicate that the present mineral may be a distinct new hydrated species with a monazite structure and a chemical composition essentially that of monazite but with silicon partly replacing phosphorus and with magnesium, calcium, and iron partly replacing the rare earths. The mode of occurrence and the mineral association suggest a low temperature hydrothermal origin for this rare-earth mineral. The possibility of heterogeneity exists and contamination by some kaolin minerals is not entirely excluded. Further work on this mineral is in progress. It is interesting to note that King (1943, p. 160) in his analysis of the pulaskite from Cnoc na Cuilean reports traces of rare earths, an observation which cannot be attributed to the rare-earth content of the accessory sphene and allanite alone. Not all the cavities contain the present rare-earth mineral. A greenish-yellow curdy mineral of the montmorillonite group has been frequently observed and stilbite has been identified from cavities of the nordmarkite from Sgor Chaonasaide.

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References.

Brögger (W. C.), 1933. Die Eruptivgesteine des Oslogebietes, VII. Skrifter Norske Vidensk.-akad. Math.-Naturv. Kl., no. 1, p. 87.

Heddle (M. F.), 1901. The Mineralogy of Scotland. Edinburgh, 2 vols.

King (B. C.), 1943. Quart. Journ. Geol. Soc., vol. 98, p. 147.

Read (H. H.), 1931. The Geology of Central Sutherland. Mem. Geol. Surv. Scotland.

Chemical variations in members of the fergusonite–formanite series.

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Summary. Attention is drawn to anomalies in the nomenclature of the niobate-tantalates, and the fergusonite series as used by Dana is renamed the fergusonite–formanite series. Chemical variations in this series are discussed with particular reference to H_2O, Ca, Ti, Yt, individual lanthanons, Th, and U. Members of the series usually show heavy lanthanons exceeding light lanthanons but one specimen shows high Gd+Tb+Dy.

Nomenclature.

THE compositional vagaries of the niobate-tantalates have, not surprisingly, led to numerous difficulties in their nomenclature. For example, the adoption of the term *series* to include minerals varying in composition between two end members is no indication that solid solution is complete or continuous in that series; and usually synthetic work is lacking. However, in the columbite–tantalite series wide variation in the Nb:Ta ratio is well established and it is reasonable to assume that Nb and Ta can similarly replace each other in a variety of minerals —indeed perhaps in all niobate-tantalates. Nevertheless, samarskites are generally assumed to have high Nb:Ta ratios whereas yttrotantalites can be held to differ compositionally from samarskites only in having low Nb:Ta ratios (although lanthanon distribution may be relevant). Mineral series in which the Nb:Ta ratios are the principal variant include the pyrochlore microlite series as well as the columbite–tantalite series. However, the fergusonite series (Dana, 1955) includes fergusonite (Nb-rich) and the variety formanite (Ta-rich) whereas the tapiolite series includes tapiolite (Ta-rich) and the variety mossite (Nb-rich). It would be better to refer to these series respectively as the fergusonite–formanite series and the mossite–tapiolite series, with mention of the Nb-rich member first. Minerals of the former series will be referred to in this paper as fergusonite-formanites when the atomic ratio Nb:Ta is unknown, fergusonites when Nb > Ta and formanites when Nb < Ta. A minor difficulty can be anticipated for a mineral

in which the determined atomic ratio Nb:Ta is, for example, $1{\cdot}00 \pm 0{\cdot}04$, where 0·04 represents the standard deviation of the analytical method employed. Such a mineral could be described as 'fergusonite (Nb:Ta = $1{\cdot}00 \pm 0{\cdot}04$)' or possibly as fergusonite/formanite.

Minerals for which the given ratio for Nb:Ta differs from 1 by the standard deviation or less could be referred to as fergusonites or formanites followed by a statement of the relevant data, e.g. 'fergusonite (Nb:Ta = $1{\cdot}03 \pm 0{\cdot}05$)' and 'formanite (Nb:Ta = $0{\cdot}98 \pm 0{\cdot}03$)'. Such examples are not likely to be common.

General chemical characteristics.

Members of the fergusonite–formanite series are chemically the least complex among the rare-earth niobate-tantalates; if only the essential elements Nb, Ta, Yt, Ln, and O are considered then they correspond to isomorphous mixtures of the two end members $Nb(Yt,Ln)O_4$ or fergusonite and $Ta(Yt,Ln)O_4$ or formanite. Analyses of typical members of the series show $(Yt,Ln)_2O_3$ and $(Nb,Ta)_2O_5$ totalling 85 % or more and prominent elements accounting for the remainder include H, Ca, U, Th, and Ti. Thus H, reported as H_2O or ignition loss, often exceeds 2 % (H_2O) and may reach 8 % in what can be regarded as slightly altered specimens. Ca is usually between 1 and 3 % CaO and doubtless substitutes for the rare-earth group, which has long been known to be rich in Yt-earths and poor in the Ce-earths (Goldschmidt and Thomassen, 1924; and Bjørlykke, 1935). U is often between 1 and 4 % but on occasions exceeds 8 %; the atomic ratio $(Yt,Ln)^{3+}:U^{4+}$ rarely falls below 8 and is generally above 15, and these moderate amounts of U may be assumed to occupy positions structurally equivalent to (Yt,Ln) positions in the original non-metamict mineral. Th varies from below 0·5 % ThO_2 to about 5 % ThO_2 but is generally up to 2 %; it substitutes for the rare earths and in Th-rich specimens the atomic ratio $(Yt,Ln)^{3+}:Th^{4+}$ may be as low as 10. Ti, substituting for Nb and Ta, is normally below 2 % TiO_2, when the atomic ratio (Nb+Ta)/Ti is 10 or more. It is possible that there are graduations between members of the fergusonite–formanite series and the variety risörite, which contains about 6 % TiO_2 and has the atomic ratio (Nb+Ta)/Ti approximately equal to 4. The type risörite contains nearly 2 % CaO and scarcely any U so the substitution of Ti might have been limited by the over-all charge conditions arising from the differing valencies between 4-valent Ti and 5-valent Nb and Ta. Nevertheless limited substitution of Ti is a characteristic not only of members of the fergusonite–formanite series

but also of samarskites and yttrotantalites where the possible additional change $Fe^{2+} \rightarrow Fe^{3+}$ might be held to favour more substantial substitution of Ti for Nb and Ta. In Ti-rich niobate-tantalates the atomic ratio (Nb+Ta)/Ti is generally below 2 and the few multiple oxide minerals containing Ti, Nb, and Ta that have values of this ratio between 2 and 4 are not confined to the same mineral species. Ti is thus only partially able to fulfil the role of Nb or Ta despite close ionic radius similarities. Synthetic studies in the system TiO_2–Yt_2O_3 $(Nb,Ta)_2O_5$ would be of particular interest in deciding the behaviour and influence of Ti.

Assuming that Yt-earths dominate throughout the fergusonite–formanite series, total rare earths are lower in formanites than in fergusonites owing to the higher atomic number of Ta. Fergusonites frequently contain over 40 % $(Yt,Ln)_2O_3$ but in the type formanite $(Yt,Ln)_2O_3$ sinks to 32 % (Simpson, 1909). Such low percentages compare with those from certain samarskites but a distinction is, perhaps, possible on consideration of the Fe contents—scarcely above a few per cent. in fergusonite-formanites and approaching 10 % or more in samarskites (and yttrotantalites).

Analytical methods and identification.

The following methods were used to obtain the data in tables I and II. Total rare-earth plus thorium oxides were determined via fluorides, perchlorates, and oxalates as previously described (Gordon *et al.*, 1949; and Butler, 1957*a*); individual rare earths were determined on the separated $(Yt,Ln)_2O_3 + ThO_2$ mixtures using an optical spectrographic method (Butler, 1957*b*), and it was confirmed from the spectrograms, using Th 4412·74 Å., that Th was below about 1–2 % in the oxides from nos. 3, 5, 7, 8 and 10, but somewhat richer in oxides from nos. 2, 6, and 9. In specimen no. 1 ThO_2 was determined by the method of Meyer and Speter (1910) and TiO_2 by the peroxide method. Oxides of Nb+Ta together were determined chromatographically (Mercer and Wells, 1954) and checked for absence of W and Ti using optical spectrographic methods; individual Nb and Ta oxides were determined on the separated $(Nb,Ta)_2O_5$ using an A.R.L. Production X-ray Quantometer and calibrating against mixed oxide standards. Optical spectrograms were recorded of minerals nos. 2–10 (and of numerous other rare-earth niobate-tantalates) using operating conditions as for individual rare-earth determination but using Ilford N. 30 photographic plates $10'' \times 4''$ and recording in the range 3600–2500 Å. with a Hilger large quartz prism spectrograph (E742) giving a plate

separation of 1 mm. for lines differing in wave number by 40. Chemically analysed minerals including type specimens were used as standards and the following additional semi-quantitative data were obtained: CaO was below 2 % throughout; Fe was below 1 % for nos. 2–6 and 8–10 but a little above 1 % for no. 7; TiO_2 was below 3 % for nos. 2 5 and 8–10, and between 3 % and 6 % for nos. 6 and 7; Al_2O_3 was below 1 % throughout; SiO_2 was below 2 % for nos. 2–6, 8, and 10, but appreciably above 2 % in nos. 7 and 9; U was highest in no. 7 which contained approximately $3\frac{1}{2}$ % U (anal. Mountain, 1935); Zr was below 1 % in all specimens except for no. 7, which contains major quantities of Zr. Table I shows analytical data for ten members of the fergusonite–formanite series arranged in order of decreasing $(Yt,Ln)_2O_3+ThO_2$. All the minerals except no. 10 give X-ray diffraction patterns closely similar to each other after suitable heat-treatment (Berman, 1955). That for the Ta-rich specimen no. 10 gave a pattern difficult to correlate with the others but with affinities to those of a heated yttrotantalite from Ceylon and a Ta-rich samarskite (or an yttrotantalite with marked Gd+Tb+Dy enrichment in the lanthanons) from Mtoko district, Southern Rhodesia. Specimen no. 10 is considered to be formanite rather than yttrotantalite on account of its chemical composition, especially its low Fe content (below 1 %).

It is considered that the data in table I together with subsidiary X-ray and optical spectrographic data are sufficient to confirm that all the specimens nos. 1–10 are members of the fergusonite–formanite series. The low partial total in table I for sample no. 6 is due to appreciable Ti and that for no. 9 is due to silicate contamination (which will not affect rare-earth distribution or the Nb:Ta ratio). Specimen no. 7 is part of that collected by Prof. E. Mountain (1935) and described as embedded in 'grey or greyish brown matrix which on analysis proves to be a form of zircon'; we have confirmed the high Zr and Si content but see no lines of zircon in the X-ray photograph.

Niobium and tantalum variations.

Specimens nos. 1–9 inclusive are all Nb rich (table I) with the fergusonites from Nedenäs (no. 6) and Boksput (no. 7) nearest to the theoretical Nb-pure end member in the series. The atomic ratio Nb:Ta remains above 23 for specimens nos. 2, 3, and 9 but drops below 9·0 for the remaining fergusonites. The latter may be regarded as fergusonites containing moderate amounts of Ta. No mineral shows Nb:Ta between, say, 5 and $\frac{1}{5}$ and there is no example here of a formanite

TABLE I. Analytical data for members of the fergusonite–formanite series. Total rare-earth oxides (of formula shown) plus thoria, niobium plus tantalum oxides, and ignition loss determined chemically as wt. % on mineral basis. Individual rare earths were determined spectrographically in and on the basis of chemically separated rare earth plus thorium oxides for nos. 1–10 (Sc_2O_3 and Eu_2O_3 below 0·1 % throughout, La_2O_3 below 0·1 %, and Pr_6O_{11} below 0·3 % where indicated by *. No data for Ho_2O_3). R^{3+}, ionic radii (Å.) of trivalent rare-earth cations. $\hat{\sigma}$, percentage standard deviations of estimate of individual rare earths for duplicate spectrograms (cols. 1–10); for bracketed values $\hat{\sigma}$ is increased by up to $\sqrt{2}$.

	R^{3+}	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	$\hat{\sigma}$.	11.
$(Yt,Ln)_2O_3$ + ThO_2 ...	—	43·30	42·60	42·42	42·35	41·43	40·33	37·16	35·76	33·91	31·04	—	31·33
$(Nb,Ta)_2O_5$	—	n.d.	42·14	47·44	45·91	44·20	38·88	37·15	51·36	35·19	55·42	—	52·10
Ign. loss	—	n.d.	2·95	1·31	1·77	2·92	3·79	2·71	5·70	5·52	n.d.	—	—
Sum	—	43·30	87·69	91·17	90·03	88·55	83·00	77·02	92·82	74·62	86·46	—	88·23
Nb:Ta (at.)	—	n.d.	24	28	6·7	8·8	30	33	6·2	26	0·07	—	0·09
Yt_2O_3	0·92	54·1	55·0	59·9	64·4	57·1	58·0	56·3	63·5	47·0	62·0	5	63·8
La_2O_3	1·14	*	0·10	*	0·15	*	*	*	*	0·21	*	7	0·36
CeO_2	1·07	0·83	0·67	0·76	1·60	0·20	0·47	0·71	(0·4)	1·05	0·79	7	0·72
Pr_6O_{11}	1·06	*	*	0·39	0·68	*	*	0·33	*	0·55	0·42	7	0·51
Nd_2O_3	1·04	2·24	1·18	1·90	5·89	1·03	0·96	1·92	0·56	2·67	2·38	5	2·06
Sm_2O_3	1·00	1·90	(1·38)	2·28	6·50	(1·7)	(1·15)	1·86	(0·6)	3·56	2·19	5	3·08
Gd_2O_3	0·97	5·95	4·55	5·50	10·2	5·20	3·62	4·90	2·11	8·17	2·52	$6\frac{1}{2}$	3·12
Tb_4O_7	0·93	1·09	1·18	1·27	1·73	1·51	0·90	1·14	(0·7)	1·78	(0·7)	6	0·62
Dy_2O_3	0·92	7·94	6·95	8·65	8·11	10·5	5·56	7·35	4·73	10·5	3·60	5	3·98
Er_2O_3	0·89	7·77	9·46	7·94	1·80	11·6	7·25	8·38	7·50	7·45	4·48	13	5·43
Tm_2O_3	0·87	1·01	1·18	1·00	(0·16)	1·07	0·90	1·02	1·10	0·77	0·88	7	1·45
Yb_2O_3	0·86	(14·4)	10·1	6·83	1·30	7·35	12·5	10·7	15·9	8·58	15·8	5	9·77
Lu_2O_3	0·85	0·86	1·29	0·82	(0·24)	0·93	1·05	1·28	1·55	0·83	1·7	20	2·06
ThO_2	—	6·10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	—	—
Sum	—	104·19	93·04	97·24	102·76	98·19	92·36	95·89	98·65	93·12	97·46	—	—

containing moderate amounts of Nb—both the Cooglegong (no. 10) and Marble Bar (no. 11) formanites have Ta exceeding Nb by at least 10 to 1 on an atomic basis. There is a large range in Nb:Ta ratios not met with in these or other members of the fergusonite–formanite series recorded in the literature. This is in contrast to the reasonably wide variation for the atomic ratio Nb:Ta recorded in samarskites: for example, from Mt. Painter, South Australia, 31 (Kleeman, 1946); from Ta-fang-Shên, south Manchuria, 11 (Takubo, 1952); and from Ryujomen, Korea, 3·4 and 1·2 (Imori and Hata, 1938). Moreover, typical atomic ratios Nb:Ta for yttrotantalites are 0·86 from Berg, Norway (Brøgger, 1906); 0·50 from Sweden (the authors, unpublished); and 0·35 from Minas Gerais, Brazil (Peixota and Guimarães, 1953). These data suggest that it will be worth while comparing Nb:Ta ratios from associated fergusonite and samarskite. It would also be useful to know comparative ratios for the associated pairs fergusonite–columbite and formanite–tanteuxenite.

Theoretically the ratio $(Nb,Ta)_2O_5$:$(Yt,Ln)_2O_3$ should widen as the Nb:Ta ratio increases (provided Yt remains the dominant rare earth) but such a correlation is difficult to see for minerals nos. 1–9 even allowing for approximate ThO_2 estimates. Nor is there any clear trend for the ratio Nb:Ta with changing Yt content as, for example, Yt in total rare earths.

Rare-earth variations.

Table I shows the individual rare earths (determined spectrographically) in the total rare earth plus thorium oxides separated from the

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1. Fergusonite–formanite, North Carolina, U.S.A. (ThO_2 = 2·77 %, TiO_2 = 2·20 %).
2. Fergusonite, var. risörite, Gryting, near Risør, Norway.
3. Fergusonite, Ceylon.
4. Fergusonite, Julianehaab, Greenland (B.M. 26899).
5. Fergusonite, Rullandsdalen, nr. Risør, Norway (G.M., Oslo; T. Tørjesen, Nov. 1923).
6. Fergusonite, var. risörite, Nedenäs, Norway (B.M. 1911, 198).
7. Fergusonite, intimately mixed with a form of zircon, Boksput farm, south-west corner of Gordonia, South Africa (B.M. 1931, 448, pres. E. D. Mountain).
8. Fergusonite, Rakwana, Ceylon (B.M. 67650 g.).
9. Fergusonite, var. tyrite, Helle, Arendal, Norway (B.M. 55162).
10. Formanite, Cooglegong, Western Australia.
11. Formanite, Marble Bar district, Western Australia. Anal. Wylie (1954); sum includes TiO_2 = 2·50 % and U_3O_8 = 0·30 %; ThO_2 = 0·13 % and Fe_2O_3 < 0·1 %; Ho_2O_3 = 1·12 %, La, Gd, Tb, and Lu values are approximate and Eu_2O_3 = tr.

minerals nos. 1–10. It will be seen that the totals vary between 92 and 104 %; this is owing to lack of data for Ho (possibly 1 % and above throughout) and Th, which lead to low summations, and to errors in the spectrographic analysis, which lead to either high or low summations. Yt is the dominant rare earth throughout and on an atomic basis varies between 63 % (no. 9) and 75 % (nos. 8 and 10) in the total rare earths, excluding Ho. This variation is small and there is no indication of any correlation between the Yt content and that of any other constituent.

TABLE II. Atomic percentages of lanthanons in total lanthanons. Nos. 1–10 on an Ho-free basis; no. 11 Ho = 3·23 % (Wylie, 1954). Localities as in table I (*Z*, atomic number).

	Z.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
La	57	—	0·30	—	0·43	—	—	—	—	0·52	—	1·21
Ce	58	2·04	1·93	2·20	4·35	0·53	1·52	1·88	1·27	2·45	2·46	2·41
Pr	59	—	—	1·14	1·87	—	—	0·88	—	1·30	1·31	1·53
Nd	60	5·70	3·48	5·60	16·4	2·80	3·17	5·20	1·82	6·40	7·57	6·70
Sm	62	4·67	3·96	6·50	17·5	4·5	3·38	5·33	1·88	8·25	6·72	9·62
Gd	64	14·1	12·3	15·8	26·4	13·2	11·1	12·3	6·39	18·2	7·52	9·39
Tb	65	2·49	3·12	3·37	4·32	3·69	2·66	2·77	2·04	3·82	2·0	1·84
Dy	66	18·3	18·5	23·0	20·4	25·8	16·5	17·9	13·9	22·6	10·3	11·7
Er	68	17·4	24·6	20·6	4·41	27·8	21·0	24·3	21·4	15·7	12·5	15·3
Tm	69	2·22	3·03	2·56	0·39	2·53	2·58	2·40	3·10	1·60	2·42	4·38
Yb	70	31·3	25·4	17·2	3·00	17·0	35·1	24·7	44·0	17·5	42·6	27·1
Lu	71	1·85	3·19	2·02	0·56	2·14	2·92	2·34	4·25	1·68	4·55	5·55

Variation amongst the lanthanons is, however, appreciable as seen in table II showing the atomic percentage of lanthanons in total lanthanons excluding Ho. The variation is greatest towards the ends of the lanthanon series and least for Gd, Tb, and Dy. The small variation in Dy, with an identical ionic radius to that of Yt, is to be expected in view of the narrow Yt variation. The total of Gd + Tb + Dy also varies modestly from 20 % in no. 10 to 51 % in no. 4 and, therefore, the minerals as a group are not particularly enriched in the middle lanthanons. Eu is below sensitivity (0·1 % Eu_2O_3 in the oxides) throughout, concurring with the low content found for Eu in fergusonites by Semenov and Barinsky (1958). Wylie (1954), however, originally reported 5·7 % Eu in lanthanons from a Western Australian formanite but has later amended his figure, as an ion exchange separation confirmed the general trends of the rare-earth distribution given, but showed the spectrophotometric values for Eu and La to be in error; preferred values are Eu = tr. and La = approx. 1 % (Dr. Wylie, personal communication). Wylie's amended data are given in table II, col. 11, and it will be

observed that reasonable agreement obtains for lanthanon distribution and values in this formanite and in the one analysed here (table II, col. 10) which has a similar Ta content and also comes from Western Australia.

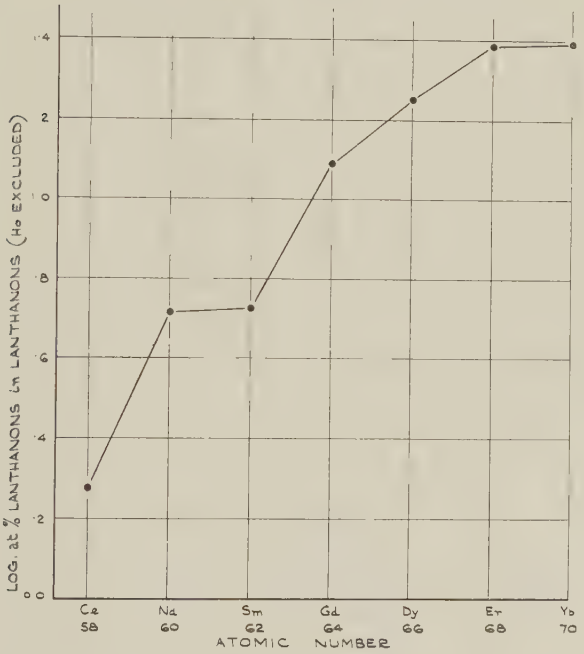

Fig. 1. Lanthanon distribution in fergusonite, Boksput farm, south-west corner of Gordonia, South Africa (B.M. 1931, 448).

Yb is the most abundant lanthanon (on an atomic basis) in minerals nos. 1, 2, 6, 7, and 10; indeed in the latter two samples it is nearly as abundant as all the remaining lanthanons taken together. Fig. 1 shows the relationship between lanthanon concentration and atomic number for the fergusonite from Gordonia, South Africa (no. 7). The distribution pattern shows the impoverishment of Ce and the tenfold concentration build-up to the peak concentration of Yb with Er almost as abundant. The distribution pattern is typical for fergusonites in that a reasonably 'smooth curve' results from the joining of the points representing *Z*-even lanthanon abundance—with the exception of Sm which is known to be nearer Gd than Nd in abundance in the lithosphere. A smooth distribution pattern in itself might not mean very much. A mineral which shows

a high degree of intolerance (like samarskite or thortveitite) to lanthanon ions outside a limited size range will give a smooth pattern irrespective of the composition of the fluid from which it crystallized; a mineral able to accept into its lattice the whole ionic size range of the lanthanons

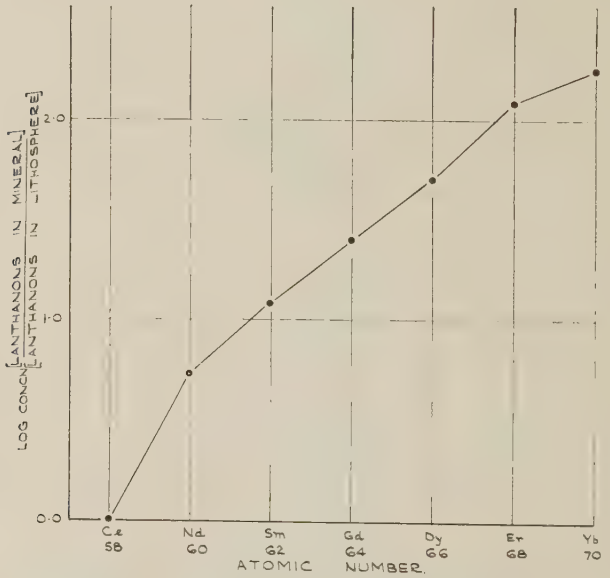

Fig. 2. Lanthanon distribution (Ce ratio taken as 1·00) in fergusonite of fig. 1 compared with that in the lithosphere.

(like yttrotungstite or gadolinite) will give a smooth distribution pattern only if that for the lanthanons in the mother fluid is smooth. Members of the fergusonite–formanite series clearly have moderately strong selectivity for the heavier lanthanons (nos. 1, 2, 6, 7, 8, and 10) and it is therefore hazardous to conclude much about the composition of the mother fluids except to suggest that they are not the result of the removal of the middle lanthanons Sm and Gd from a fluid containing lanthanons proportionately abundant as in the average lithosphere. This is brought out in fig. 2, which shows a plot of atomic number against the ratio of the atomic abundance of the *Z*-even lanthanons in fergusonite no. 7 to that in the lithosphere (Suess and Urey, 1956). When the points are joined a reasonably smooth curve without depressions or minima for Sm or Gd results. Reasonably similar curves are obtained for specimens nos. 1, 2, 6, and 8. Formanite no. 10 shows the

highest Yb enrichment of the samples analysed and the distribution pattern is shown in fig. 3; compared with the other samples it could be described as rich in Nd and poor in Sm, Gd, and Dy. Fig. 4, however, shows the concentration of the lanthanons in the mineral relative to

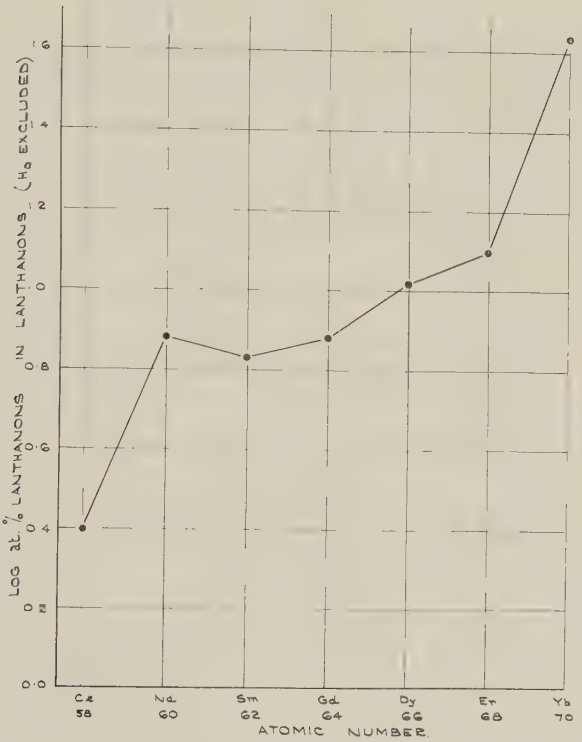

FIG. 3. Lanthanon distribution in formanite, Cooglegong, Western Australia.

that in the average lithosphere and the arrangement of the points suggests that the formanite may have crystallized from an environment poor in Gd and Dy (and Er) rather than from one enriched in Nd and Sm relative to Ce. Such a suggestion presupposes that formanite does not tend to concentrate Sm as well as Yb and exclude lanthanons with intermediate sizes (e.g. Gd and Dy); but it seems unlikely that formanites will concentrate lanthanons in a way peculiar to davidite (Dixon and Wylie, 1951, and unpublished work by the authors) whereas fergusonites do not. Also shown in fig. 4 is the plot from the data of Wylie (table II,

col. 11) on formanite from Marble Bar, Western Australia. The curves are strikingly similar and it is suggested that both the Cooglegong and the Marble Bar formanites have a similar paragenesis.

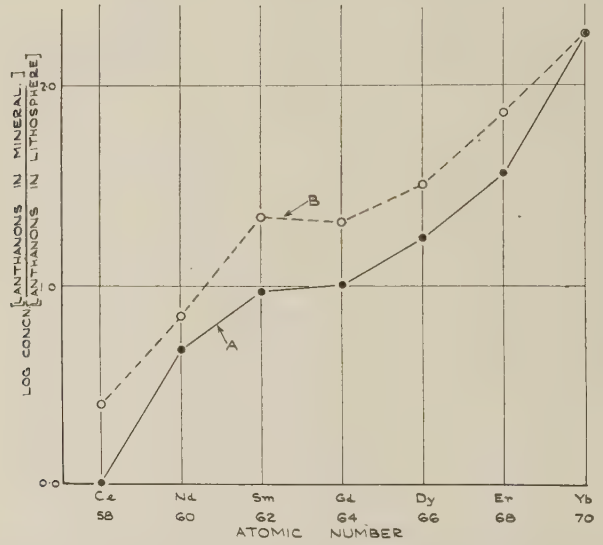

Fig. 4. Lanthanon distribution in formanite of fig. 3 (A with Ce ratio taken as 1·00) and formanite, Marble Bar, Western Australia (B with log Ce ratio taken as 0·20); after Wylie (1954), each compared with that in the lithosphere.

Peak Yb concentration has been observed by Semenov and Barinsky (1958) in their recent informative paper. Using X-ray methods they analysed seven members of the fergusonite–formanite series (all described as fergusonite but without data on Nb or Ta) and found Yb the commonest lanthanon throughout. This is so whether their figures are taken to refer to wt. % or to atomic %. Distribution patterns for their fergusonite–formanite from Iveland, Norway (no. 65), and those for minerals nos. 1, 2, 6, 7, 8, and 10 in this paper are broadly similar; that for their mineral from Sabaragamuwa, Ceylon (no. 71), resembles that for our formanite no. 10. Their remaining minerals, however, show Ce exceeding Nd. In their specimen from Evje, Norway (no. 70), Ce is nearly five times the concentration of Nd (fig. 5), which indicates that either the mother fluids were exceptionally rich in Ce with respect to Nd or that certain members of the fergusonite–formanite series are able to incorporate Ce into the lattice with appreciably greater ease than Nd.

Incidentally Semenov and Barinsky show eight out of twelve members of the euxenite–polycrase series with Ce more abundant than Nd (3 samples from the same locality) and this is also in contrast to the findings of Bjørlykke (1935) and Butler (1958). Curiously, of the thirteen

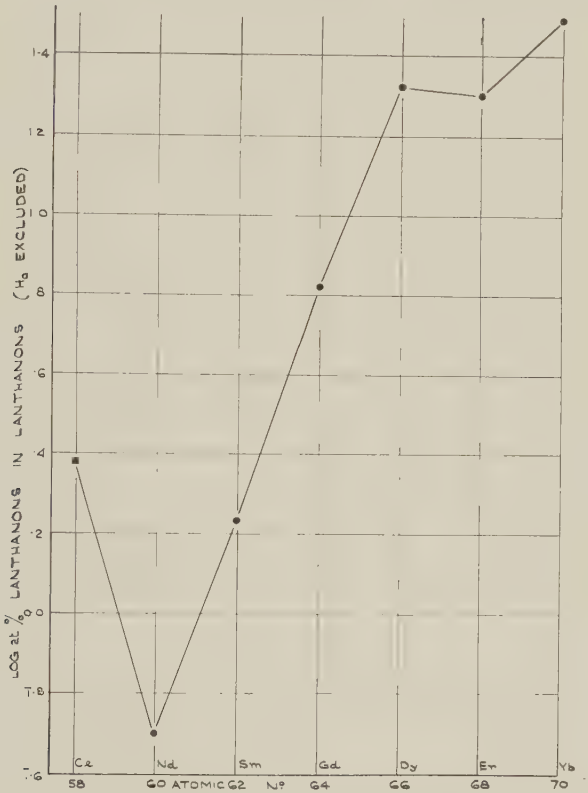

Fig. 5. Lanthanon distribution in fergusonite-formanite, Evje, Norway, after Semenov and Barinsky (1958).

gadolinites analysed only three show Ce more abundant than Nd and yet gadolinite is a complete-assemblage type mineral whilst members of both the fergusonite–formanite series and the euxenite–polycrase series are held to be selective towards the heavier lanthanons.

Fig. 6 shows the lanthanon distribution in the fergusonite from Rullandsdalen, Norway (No. 5), and it is seen that Er is more abundant than Yb. Roughly similar distribution curves obtain for fergusonites

nos. 3 and 9 except that Dy is the most abundant lanthanon. The peak uptake of Dy and Er may be due to the low availability of the heavier lanthanons. Alternatively or additionally the average ionic size of the most easily admitted lanthanon size range in the lattice may change

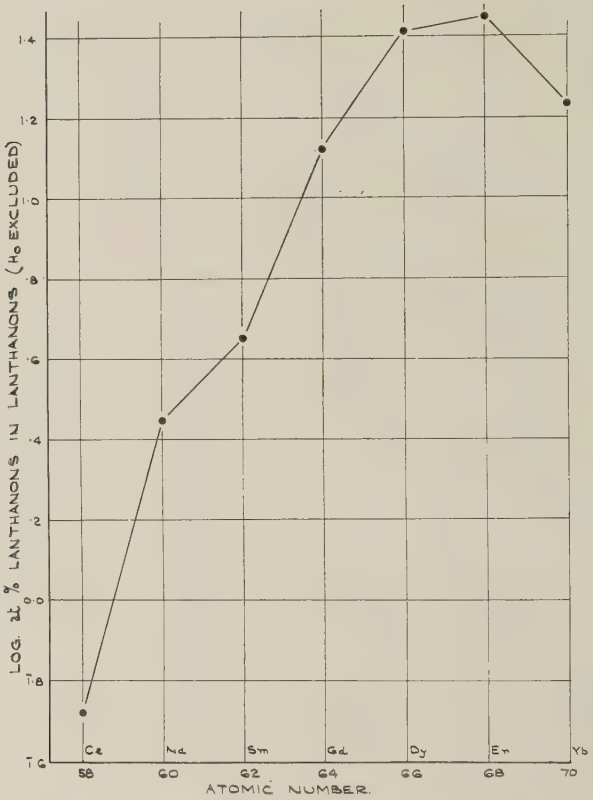

Fig. 6. Lanthanon distribution in fergusonite, Rullansdalen, near Risør, Norway.

somewhat with formational temperature of the mineral and restrict Yb uptake accordingly; unfortunately there is rather little data on the temperature range over which fergusonite can crystallize.

Fig. 7 shows the distribution of the *Z*-even lanthanons in the fergusonite from Julianehaab, Greenland (no. 4), and it is at once seen that the pattern is distinct from all those obtained for the other members of the fergusonite–formanite series. Gd is the most abundant lanthanon and even Tb exceeds Yb which is the least abundant *Z*-even lanthanon.

On an atomic basis Gd+Tb+Dy exceed 50 % in the lanthanons (Ho excluded)—a property that has tentatively been ascribed as characteristic of samarskites (Butler, 1958; and Semenov and Barinsky, 1958). Fig. 8 shows the relationship between the atomic number of the *Z*-even

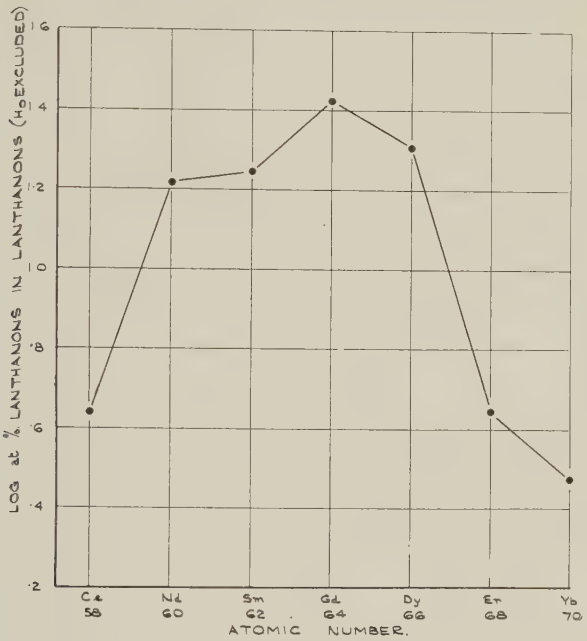

Fig. 7. Lanthanon distribution in fergusonite, Julianehaab, Greenland (B.M. 26899).

lanthanons and the ratio of concentration of the lanthanons in mineral no. 4, compared with that in the lithosphere; comparative data are plotted for a previously described samarskite from Brazil. The two curves are sensibly close even though Dy is at the summit of the curve for the samarskite. A probable explanation for the unusual lanthanon distribution in the Greenland fergusonite is that it crystallized from an environment very depleted of Er and Yb; nevertheless, the fact that fergusonite is formed indicates a tolerance to lanthanons of middle size not suspected in considering data for all the other fergusonites. The problem of the impoverishment of the heaviest lanthanons (e.g. Yb and Er) from a rare-earth assemblage by mineral crystallization remains. Thortveitite seems to be capable of concentrating Yb to an extreme

degree, but analyses of the mineral are not numerous (Goldschmidt and Thomassen, 1924; Bjørlykke, 1935; and Semenov and Barinsky, 1958). On the basis of more extensive data, xenotime and members of the euxenite–polycrase series are known to favour the heavier rather

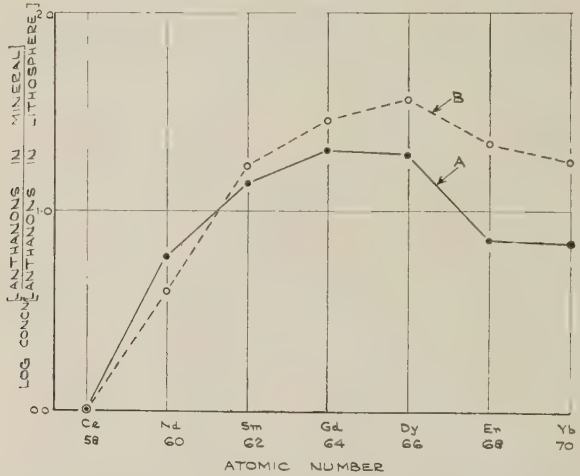

FIG. 8. Lanthanon distribution in fergusonite of fig. 7, (A) and samarskite, Divino Ubá, Minas Gerais, Brazil (B.M. 1926, 296), (B), each compared with that in the lithosphere (Ce ratio taken as 1·00).

than the lighter lanthanons (Goldschmidt and Thomassen, 1924; Bjørlykke, 1935; Semenov and Barinsky, 1958; Butler, 1958; and Carron *et al.*, 1958), but their selectivity is on a par with that of the majority of fergusonites and although the concentration ratio Yb:Er is usually above unity it can be substantially less. It is, of course, possible that other fergusonites from the Julianehaab area will show higher Yb contents, in which case mineral no. 4 would be regarded as a very late stage fergusonite crystallizing from an environment low in Yb and Er due to prior crystallization of more 'normal' fergusonites. It would clearly be valuable to study a number of fergusonites occurring in petrogenetically connected pegmatites and this we propose to do in the future.

Acknowledgements. We wish to thank the curators of H.M. Geological Museum, the British Museum (Natural History), and the Geologisk Museum (Oslo) for providing specimens and the Director of Rothamsted Experimental Station for the loan of the spectrograph used for rare-earth determinations. We have benefited greatly from discussions with J. E. Horne of H.M. Geological Survey (Atomic Division) and would record our thanks.

References.

Berman (J.), 1955. Amer. Min., vol. 40, p. 805 [M.A. **13**–260].

Bjørlykke (H.), 1935. Norsk Geol. Tidsskr., vol. 14, p. 211 [M.A. **6**–214].

Brøgger (W. C.), 1906. Skrifter Vidensk.-Selsk. Christiania, Math.-naturv. Klasse, no. 6, p. 92.

Butler (J. R.), 1957*a*. Geochimica Acta, vol. 12, p. 190.

—— 1957*b*. Spectrochimica Acta, vol. 9, p. 332 [M.A. **13**–573].

—— 1958. Min. Mag., vol. 31, p. 763.

Carron (M. K.), Naeser (C. R.), Rose (H. J., Jr.), and Hildebrand (F. A.), 1958. U.S. Geol. Survey Bull. 1036–N, p. 253 [M.A. **14**–37].

Dana (J. D.) and Dana (E. S.), 1955. The system of mineralogy. 7th edn, ed. Palache (C.), Berman (H.), and Frondel (C.). Wylie & Sons, 1955.

Dixon (P.) and Wylie (A. W.), 1951. Nature, London, vol. 167, p. 526 [M.A. **11**–541].

Goldschmidt (V. M.) and Thomassen (L.), 1924. Skrifter Vidensk.-selsk. Kristiania, I. Mat.-naturv. Kl., no. 5 [M.A. **3**–261].

Gordon (L.), Vanselow (C. H.), and Willard (H. H.), 1949. Anal. Chem., vol. 21, p. 1323.

Imori (Satoyasu) and Hata (Shin), 1938. Sci. Papers Inst. Phys. Chem. Res. Tokyo, vol. 34, p. 922.

Kleeman (A. W.), 1946. Trans. Roy. Soc. South Australia, vol. 70, p. 175 [M.A. **10**–545].

Mercer (R. A.) and Wells (R. A.), 1954. Analyst, vol. 79, p. 339.

Meyer (R. J.) and Speter (M.), 1910. Chem. Zeitung, vol. 34, p. 306.

Mountain (E. D.), 1935. Records Albany Museum, vol. 4, p. 122.

Peixota (F.) and Guimãraes (D.), 1953. Escola de Engenharia, Univ. Minas Gerais, Inst. de Pesquisas Radioativas, Pub. no. 1, 35 pp. [M.A. **12**–279].

Semenov (E. I.) and Bakinsky (R. L.) [Семенов (Е. И.) и Баринский (Р. Л.)], 1958. Geochemistry (translation of Russian periodical Геохимия), 1958, no. 4, p. 398.

Simpson (E. S.), 1909. Proc. Australasian Assoc. Adv. Sci., vol. 12, p. 310.

Suess (H. E.) and Urey (H. C.), 1956. Review Mod. Physics, vol. 28, p. 53.

Takubo (Jitsutarô), 1952. Journ. Geol. Soc. Japan, vol. 58, p. 203 [M.A. **12**–112].

Wylie (A. W.), 1954. Amer. Min., vol. 39, p. 667 [M.A. **12**–579].

Two synthetic compounds containing chromium in different valency states.

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Summary. Two compounds, one an apatite and the other a perovskite, have been synthesized by sintering mixtures containing CaO and Cr_2O_3, and CaO, Cr_2O_3, and Fe_2O_3 respectively. The apatite formed by partial oxidation of the Cr_2O_3 and subsequent pick-up of moisture from the atmosphere, to give $Ca_5(CrO_4)_3OH$. The perovskite formed as a non-stoicheiometric compound $Ca_4(Fe,Cr)_4O_{11}$ by partial oxidation of the Cr_2O_3 during firing. Lattice parameters and interplanar spacings are given for the two structures.

IT is well known that Al_2O_3 can replace Fe_2O_3 in dicalcium ferrite to form a calcium alumino-ferrite up to a limiting composition of 6·37CaO.2·28 Al_2O_3.Fe_2O_3 (Newkirk and Thwaite, 1958). In the course of work on used chrome-magnesite roof bricks Cockbain and Johnson (1958) found an intergrowth of dicalcium ferrite and calcium silicophosphate (originally liquid) in regions adjacent to the hot face. Hence an investigation into the limits of Cr_2O_3 substitution in dicalcium ferrite or alumino-ferrite was considered necessary in order to assess the composition of the liquid phase in the brick and the mechanism of selective removal of Al_2O_3 and Cr_2O_3 from the chrome spinel grains.

During the course of synthesizing such mixtures two new compounds were discovered both containing tri- and hexavalent chromium. The first was found in mixtures, fired at 1200° C. in air, containing more than about 10 % substitution of Cr_2O_3 for Fe_2O_3 in dicalcium ferrite. This phase became more dominant with increasing substitution till at 40 % it was the only constituent present. X-ray powder data indicated it to be a perovskite-type compound isomorphous with $GdFeO_3$ as reported by Geller (1956) with an orthorhombic unit cell but having *a* 5·415 Å., *b* 5·489 Å., *c* 7·480 Å.

The oxidation of Cr_2O_3 in mixtures of high basicity is well known and our work indicates that only 10 % substitution of Fe_2O_3 by Cr_2O_3 is possible before oxidation begins to occur in air. If complete oxidation

of the Cr_2O_3 to CrO_3 occurred then one would expect the $33\frac{1}{3}$ % substitution mixture to give a single phase. This can be expressed clearly by the equation:

$$2CaO.\tfrac{2}{3}Fe_2O_3.\tfrac{1}{3}Cr_2O_3 + O \rightarrow 2CaO.\tfrac{2}{3}Fe_2O_3.\tfrac{2}{3}CrO_3 = 3CaO.Fe_2O_3.CrO_3 = 3CaMO_3,$$

where M is a random mixture of Fe^{3+} and Cr^{6+} in the ratio 2:1, giving a mean valency of 4 and hence the isomorphism with perovskite, $CaTiO_3$.

TABLE I. X-ray powder data, obtained with Co-$K\alpha$ radiation on a Guinier type focusing camera.

Perovskite-type structure. $Ca_4(Fe,Cr)_4O_{11}$.

hkl.	$d_{obs.}$	*I.*	$d_{calc.}$	*hkl.*	$d_{obs.}$	*I.*	$d_{calc.}$
110	3·863	m	3·858	—	1·916	w	—
*002	3·745	mw	3·740	*004	1·868	ms	1·870
*020	2·740	ms	2·745	221			1·868
*200	2·710	s	2·707	132	1·567	m	1·573
112	2·684	vs	2·684	312	1·561	m	1·559
003	2·495	w	2·493†	024	1·540	mwb	1·545
022	2·217	w	2·212	204			1·539
202	2·193	w	2·192	*040	1·375	w	1·372
—	2·157	vw	—	*400	1·353	wb	1·354
220	1·928	s	1·927	224	1·341	mw	1·342

$d_{calc.}$ from a 5·415 Å., b 5·489 Å., c 7·480 Å. Probable space-group *Pbnm*.

* Used to calculate a, b, and c.

† 003 not permitted by *Pbnm*, which with the other two unindexed lines perhaps indicates a bigger unit cell or some ordering of the structure.

Chromium analogue of apatite. $Ca_5(CrO_4)_3OH$.

hkl.	$d_{obs.}$	*I.*	$d_{calc.}$	*hkl.*	$d_{obs.}$	*I.*	$d_{calc.}$
100	8·38	mw	8·38	221	2·287	w	2·286
101	5·37	mw	5·37	311	2·206	w	2·204
110	4·835	w	4·834	222	1·990	ms	1·990
200	4·193	w	4·186	213	1·879	ms	1·880
111	3·978	m	3·981	321	1·850	mw	1·853
201	3·597	vw	3·595	410	1·827	wb	1·827
002	3·504	s	3·505	402	1·798	wb	1·797
102	3·242	w	3·235	004	1·752	wb	1·753
210	3·162	m	3·164	322	1·683	w	1·684
211	2·888	vs	2·884	313	1·645	vw	1·647
112	2·838	ms	2·838	420	1·579	vw	1·582
300	2·791	s	2·791	214	1·542	vw	1·533
202	2·688	ms	2·687	502	1·511	mw	1·511
301	2·595	w	2·593	304	1·482	wb	1·484
310	2·323	mw	2·322	511	1·469	vw	1·470

$d_{calc.}$ from a 9·67$_7$ Å., c 7·01 Å., c/a 0·725. Apatite space-group $P6_3/m$.

Actually, the single-phase region is found near to the 40 % substitution level. This, together with the chemical analysis (CaO 40·5, Fe_2O_3 34·25, Cr_2O_3 12·3, CrO_3 12·4 %, sum 99·45 %), indicates the perovskite to be non-stoicheiometric (oxygen deficient). Its formula is very near to $Ca_4(Fe,Cr)_4O_{11}$, i.e. half-way between dicalcium ferrite $Ca_4Fe_4O_{10}$ and the ideal perovskite $Ca_4M_4O_{12}$. The presence of Cr^{6+} in perovskites has been suggested by Roy (1954), and the recent work of Bertaut, Blum, and Sagnières (1959) on dicalcium ferrite shows clearly the relationship between the two compounds. A comparison of the structures shows the metal atoms and all but two of the oxygen atoms virtually unchanged in position and a shift through about a quarter of a cell of these two oxygen atoms leaves a hole which can accommodate the extra one or two oxygens demanded by the perovskite formula.

The second compound was discovered whilst synthesizing similar mixtures containing only CaO and Cr_2O_3. It is an apatite-type structure with a hexagonal cell having a 9·67 Å. and c 7·01 Å. This phase was formed in mixtures containing CaO and Cr_2O_3 in the molecular ratio of 10:3 when heated in ordinary air at 950° C. It did not form in dry air. Considering the results of Korber and Trömel (1933) on mixtures of $4CaO.P_2O_5$ and $3CaO.P_2O_5$, which gave hydroxyapatite $Ca_5(PO_4)_3OH$ on heating, it seems likely that these chromium-containing mixtures also picked up moisture and formed a hydroxyapatite. Minguzzi (1941) reports small amounts of tri- and hexavalent chromium in solid solution with phosphate apatites and recent work by Glasser and Osborn (1958) has shown that the compound $9CaO.4CrO_3.Cr_2O_3$ is isomorphous with β-$Ca_3(PO_4)_2$. Here the mixture of tri- and hexavalent chromium in the ratio of 1:2 gives a mean valency of 5, thus being equivalent to the pentavalent phosphorus. Hence using this equivalence of phosphorus and chromium in these compounds the formula can be written as $Ca_5(CrO_4)_3OH$ or as $10CaO.4CrO_3.Cr_2O_3.H_2O$ (by analogy with the 9:4:1 compound). This is confirmed by chemical analysis, which gave CaO 49·5, Cr_2O_3 13·25 (by difference), CrO_3 35·6, H_2O 1·65 % (loss at 900° C.), sum 100·00 %.

Experimental details. The first compound was prepared from $CaCO_3$, Cr_2O_3, and ferrous oxalate by mixing in the correct proportions. The sample was initially fired to 1000° C. for 1 hour to decompose the carbonate and oxalate followed by grinding for 20 minutes. It was then rammed into pills and fired for 4 hours at 1200° C. in air. After photographing, each sample was reground, pressed, and refired at 1200° C. for a further 4 hours and then rephotographed.

The second compound was made from $CaCO_3$ and Cr_2O_3 and treated similarly, but heated in pill form for 24 hours at 900° C.

Acknowledgement. The author is indebted to Mr. F. H. Saniter, Director of Research, for permission to publish these results.

References.

Bertaut (F. F.), Blum (P.), and Sagnières (A.), 1959. Acta Cryst., vol. 12, p. 149.
Cockbain (A. G.) and Johnson (W.), 1958. Trans. Brit. Ceram. Soc., vol. 57, p. 511.
Geller (S.), 1956. Journ. Chem. Physics, vol. 24, p. 1236.
Glasser (F. P.) and Osborn (E. F.), 1958. Journ. Amer. Ceram. Soc., vol. 41, no. 9, p. 358.
Körber (F.) and Trömel (G.), 1933–4. Archiv Eisenhuttenwesen, vol. 7, p. 7.
Minguzzi (C.), 1941. Periodico Min., vol. 19, p. 343.
Newkirk (T. F.) and Thwaite (R. D.), 1958. Journ. Res. Nat. Bur. Stand., vol. 61, p. 233, R.P. 2900.
Roy (R.), 1954. Journ. Amer. Ceram. Soc., vol. 37, no. 12, p. 581.

A minor occurrence of sepiolite from Puyvalador, near Quérigut, France.

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[Taken as read 28 January 1960.]

Summary. Sepiolite found as a minor constituent of dolomitic marble bordering tremolite rock from the southern contact zone of the Quérigut granite is briefly described and optical data are presented. A possible paragenesis, following on break-down of the tremolite under the action of carbon dioxide, is suggested.

WHILE studying a series of zoned skarn rocks from near Puyvalador, on the southern boundary of the Quérigut granite, France (Watters, 1958), the writer examined a tremolite-rich rock that had been collected on a previous expedition by members of the Department of Mineralogy and Petrology, Cambridge. The rock, which was found in the quarry 400 metres north of the road junction RN 118 D 32 (Watters, 1958, p. 707), shows a compact mass of pale green tremolite with an irregular contact against a light brownish fine-grained marble.[1] In one specimen an indistinct zonation is visible, the more or less pure tremolite rock being separated from the marble by a thin layer, 7 to 10 mm. wide, of tremolite and carbonate. The sepiolite was recorded in one part of the rock in a narrow indistinct area in the marble close to the boundary with the tremolite. It is visible only under the microscope, and is found as tiny irregular patches or occasionally as little vein-like areas within the marble (fig. 1).

The tremolite (β 1·617 to 1·618 $\pm$0·003) occurs in irregular prismatic grains reaching up to about 2 mm. long. In thin section (61259)[2] it is colourless and is seen to be accompanied by occasional little ragged flakes of phlogopitic mica (β 1·594 to 1·598 $\pm$0·003, α very pale yellow-green, γ pale greenish brown). Near the boundary with the marble the larger tremolite crystals may be partly or completely crossed by narrow

[1] The presence of both calcite and dolomite was shown by the staining of several uncovered slides, following the method outlined by Tilley (1920, p. 452), as well as by comparison of ω for both minerals in refractive index liquids.

[2] The number refers to the catalogued specimen in the Harker collection, Department of Mineralogy and Petrology, Cambridge University.

irregular tongues of carbonate; in many places a number of distinct adjacent tremolite crystals have identical optical orientation and appear

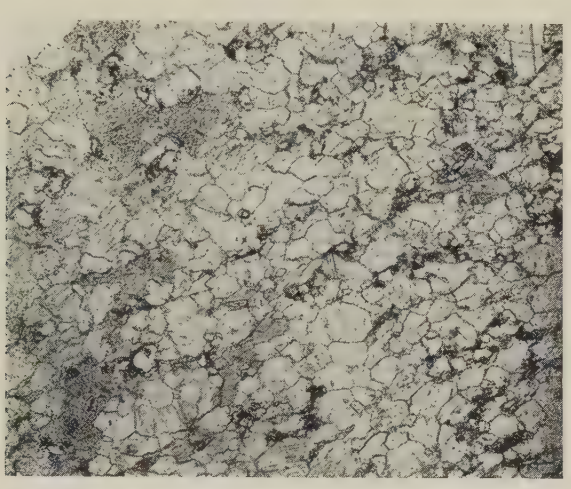

FIG. 1. Photomicrograph of dolomitic marble, near Puyvalador. Interstitial sepiolite is readily visible in the left-hand part of the photograph as irregular darker grey areas against the lighter-coloured carbonate.

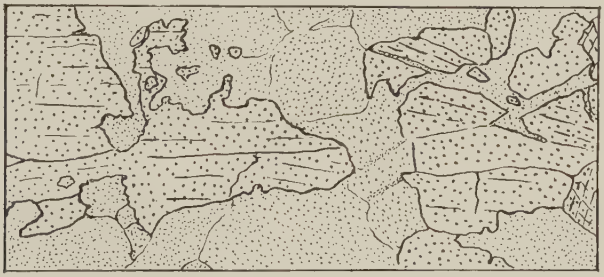

FIG. 2. Camera-lucida sketch of part of tremolite-carbonate rock (61259). Note textural relations between the tremolite and the carbonate (mainly calcite). The isolated tremolite grains on the left are in optical continuity with the large irregular crystal, which partly encloses tongue-like areas of calcite (drawn under crossed nicols, ×40).

originally to have formed a single large individual (fig. 2). The texture of the rocks strongly suggests that the tremolite here has been partly broken down and replaced by calcite or by calcite and dolomite (see below).

Properties of the sepiolite. The sepiolite was identified only after an X-ray powder photograph had been taken on grains hand-picked from an uncovered slide. The pattern indicated that the mineral is similar to a sepiolite from Brinton's quarry, Chester Co., Pennsylvania (McKinstry, 1916). The variation in the optical properties of the sepiolite in the Puyvalador rock shows that its composition is apparently not constant, but unfortunately not enough of the mineral was available for a fuller determination of its properties and for an analysis. In thin section it is colourless, varying to light yellowish or even to a distinct brownish tint (fig. 1). Much of it is isotropic but in places it shows a faint patchy birefringence (0·002 to 0·003). The colourless or light yellowish material has n between 1·550 and 1·555. On the other hand the brownish material has a lower, though variable, refractive index, and often both colour and index vary within the same grain; typical values of n for this material range between 1·509 and 1·528. Without further data it is not possible to account satisfactorily for these variations in the optical properties of the mineral.

Paragenesis. Sepiolite has been recorded from numerous localities (see, for example, Lacroix, 1893, pp. 454–460; Doelter, 1914, pp. 374–383). It is found in association with other alteration products in serpentinite bodies, as a constituent of some limestones and marls (e.g. Keeling, 1956), or in the argillaceous rocks associated with some saline deposits (Grim, 1953, p. 359). At Riverside, California, sepiolite is found filling small veins in calcite near an occurrence of chrysotile and deweylite. Daly (1935, pp. 651–652) suggests that here the sepiolite has been derived by alteration of the chrysotile and deweylite, themselves the product of alteration of epidote or diopside or both. The Puyvalador mineral is apparently found in the same type of environment as the Riverside sepiolite.

It is clear that the rock cannot have developed under similar physical conditions to the neighbouring wollastonite–grossular–clinozoisite skarns (Watters, 1958), and physical conditions in the contact region of the granite have obviously varied to a marked extent within quite short distances. The replacement of the tremolite by carbonate noted above suggests that retrograde action has taken place in the rock under discussion. It is tentatively suggested that an earlier-formed tremolite rock—possibly produced by silicification of a band of magnesia-rich carbonate—has been altered, in the presence of water, by carbon dioxide, the source of which may be sought in the decarbonation of the neighbouring limestones during the formation of the skarns (cf. Bowen, 1940,

pp. 265–266). This suggested alteration could be a source of the small amounts of sepiolite recorded in the rock. One possible reaction may be written as follows:[1]

$$Ca_2Mg_5Si_8O_{22}(OH)_2 + 3CO_2 + H_2O \rightarrow CaCO_3 + CaMg(CO_3)_2 + 4MgO.6SiO_2.2H_2O + 2SiO_2.$$

By this reaction equal amounts of calcite and dolomite are produced, but the microscopic examination indicates that the bulk of the carbonate in the tongues penetrating the tremolite crystals is calcite. Moreover, no quartz or opal was observed in the rock, and an alternative reaction involving a small amount of dolomite on the left-hand side could be suggested as follows:

$$3Ca_2Mg_5Si_8O_{22}(OH)_2 + 5CO_2 + 5H_2O + CaMg(CO_3)_2 \rightarrow 7CaCO_3 + 4[4MgO.6SiO_2.2H_2O].$$

Acknowledgements. The writer would like to thank Mr. K. Rickson for taking the X-ray powder photograph of the sepiolite. Dr. G. F. Claringbull of the British Museum (Natural History) kindly supplied a small specimen of sepiolite from Brinton's quarry, Pennsylvania (B.M. 1924, 1425). The writer is grateful for helpful comments and suggestions from Dr. H. M. Pantin, Dr. J. J. Reed, and Mr. A. Steiner.

[1] The formula for sepiolite given is that suggested by Mlle Caillère (1951, p. 231).

References.

Bowen (N. L.), 1940. Journ. Geol., Chicago, vol. 48, p. 225 [M.A. **8**–243].

Caillère (Mlle S.), 1951. *In* X-ray identification and crystal structure of clay minerals. Min. Soc., London, p. 224.

Daly (John W.), 1935. Amer. Min., vol. 20, p. 638 [M.A. **6**–224].

Doelter (C.), 1914. Handbuch der Mineralchemie, Bd. II, I (Steinkopff, Dresden and Leipzig).

Grim (Ralph E.), 1953. Clay mineralogy (McGraw-Hill, New York) [M.A. **12**–184].

Keeling (P. S.), 1956. Min. Mag., vol. 31, p. 328.

Lacroix (A.), 1893. Minéralogie de la France, Tome 1 (Baudry, Paris).

McKinstry (Hugh E.), 1916. Amer. Min., vol. 1, p. 57.

Tilley (C. E.), 1920. Geol. Mag., vol. 57, p. 449.

Watters (W. A.), 1958. Min. Mag., vol. 31, p. 703.

Thaumasite from Co. Down, Northern Ireland.[1]

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[Taken as read 28 January 1960.]

Summary. Thaumasite has been found in a dolerite sill at Ballyalton, Co. Down, Northern Ireland. Indexed powder data for the mineral are given.

THAUMASITE, a complex sulphate salt ($CaSiO_3.CaCO_3.CaSO_4.14{\cdot}5H_2O$) has been recorded from only four countries but has been the subject of numerous papers. It was first noted by Gumaelius (1874) from the sulphide Bjelke Mine at Åreskutan, Sweden, but it was not until 1878 that it was described and named by Nordenskjöld, the name being derived from the Greek *θαυμάζειν*, 'to be surprised'. Other occurrences in Sweden, in association with sulphide ore deposits, were later noted by Widman (1890), Backström (1897), and Flink (1917). The paragenesis was discussed by Aminoff (1918, 1931) and Magnusson (1924).

In 1896 Penfield and Pratt described thaumasite and other zeolites from cavities in basic lavas from Paterson and Great Notch in the Watchung Mountains area, New Jersey, U.S.A. A similar occurrence was described by Mauritz (1931) from near Plattensee, Hungary. A further occurrence at the Old Hickory Mine, Beaver Co., Utah, was described by Butler and Schaller (1911), and Schaller (1912). The thaumasite from Utah, Sweden, and Sulitelma, Norway (Vogt, 1938), is similar in its mode of occurrence as it is found in fissures in sulphide ore deposits. It is presumed by Butler and Schaller (1911), Aminoff (1918, 1931), and Vogt (1938) to have formed at a very late stage of mineralization. A different paragenesis was recorded from Crestmore, California, by Foshag (1920), Larsen and Foshag (1921), Larsen and Dunham (1933), and Dunham (1933) who described veinlets of thaumasite where limestone had been invaded by granodiorite and quartz-monzonite. Other publications that have discussed the structure

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composition, and properties of thaumasite from the known localities include papers by Allen (1915), Holden (1922), and Welin (1956).

The Irish thaumasite, which appears to be the first recorded occurrence in the British Isles, has been found in a Tertiary dolerite sill encountered in a borehole sunk 2100 yards south-west of Flush Hall, Ballyalton, Newtownards, Co. Down (1-inch Geological Sheet 37). Patches of soft white material up to 3 mm. across that coated a fracture surface were observed by Mr. A. Fowler from specimens collected at 262 feet 8 inches (G.S.M. No. N.I. 1120). Later examination showed that these patches and others from a specimen at 413 feet (N.I. 1157) consisted of thaumasite. The dolerite sill from which the specimens were obtained is intruded into Triassic sediments, which consist mainly of conglomerates and breccias.

Under the microscope the thaumasite is acicular, colourless, and uniaxial negative with $\omega = 1{\cdot}504$, $\epsilon = 1{\cdot}470$, $\omega - \epsilon = 0{\cdot}034$ for sodium light. With one exception (Penfield and Pratt, 1896), the refractive indices agree with those determined for thaumasite from other localities (Nordenskiöld, 1878; Lévy and Lacroix, 1888; Backström, 1897; Butler and Schaller, 1911; Vogt, 1938).

The occurrence is comparable with that from Paterson, New Jersey, and Plattensee, Hungary, where thaumasite is found as a late stage mineral associated with zeolites in basic rocks. Wherry (1922) has suggested that solutions which would normally deposit calcite and zeolites may react with anhydrite to form thaumasite. Both calcite and zeolites (including analcime and natrolite) are present in amygdales and cracks in the Ballyalton dolerite, and anhydrite, gypsum, and calcite occur in the adjacent Triassic sediments as a cement and in veins. The thaumasite may therefore owe its origin to the agencies suggested by Wherry.

X-ray data. X-ray powder data were obtained using Co-$K\alpha$ radiation and a Philips camera of 11·483 cm. diameter. The *d*-spacings (table I) are identical with those obtained from films of thaumasite from Burger's Quarry, West Paterson, New Jersey (G.S.M. No. M.I. 21089), but differ considerably from the figures in the X-ray Powder Data File (card 2–0061). All the diffraction lines can be satisfactorily indexed on a hexagonal cell with a 11·03 Å. and c 10·40 Å., giving an axial ratio of c/a 0·943. These cell dimensions are slightly larger than those given by Aminoff (1933) (a 10·90 Å., c 10·29 Å., c/a 0·944) and by Welin (1956) (a 10·95 Å., c 10·30 Å., c/a 0·941). The line intensities were measured with a microphotometer.

TABLE I. X-ray powder data for thaumasite from Ballyalton Borehole No. 3, Co. Down (G.S.M. No. M.I. 30218). $\lambda = 1{\cdot}7889$ Å.

*hkl.**	*d*, Å.	*I.*	*hkl.**	*d*, Å.	*I.*	*hkl.**	*d*, Å.	*I.*
100	9·56	100	113	2·935	< 1	411	2·045	< 1
101	7·04	2	220	2·755	2	322	2·019	3
110	5·51	40	302	2·713	14	412	1·934	3
111	4·88	5	310	2·649	4	500	1·911	10
200	4·76	5	004	2·599	< 1	331	1·809	6
102	4·56	6	311	2·565	10	421	1·778	3
201	4·34	4	213	2·499	10	332 006	1·733	3
112	3·78	16	312	2·357	4	511	1·692	2
210	3·61	1	204	2·282	< 1	414	1·626	4
202	3·51	6	320	2·191	6	600	1·592	4
211	3·41	20	402					
300	3·18	16	223	2·155	13 vb	430	1·570	< 1
301	3·04	< 1	321					
			313	2·106	5	431	1·551	1
			410	2·086	2	513	1·538	1
						226 107	1·467	1

* Hexagonal indices *hkil* with third index omitted.

References.

The following references are additional to the bibliography of thaumasite given by T. VOGT, Norsk. Geol. Tidsskr., 1938, vol. 18, p. 291.

HOLDEN (E. F.), 1922. Amer. Min., vol. 7, p. 12.

WELIN (E.), 1956. Arkiv Min. Geol., vol. 2, no. 5, p. 137.

WHERRY (E. T.), 1918. Proc. U.S. Nat. Mus., vol. 54, p. 373.

Note: There is a specimen of thaumasite (B.M. 1958, 88) from Embleton quarry, nr. Cockermouth, Cumberland, in the mineral collection of the British Museum (Natural History). Several pieces, about 2–3 cm. across and consisting of a mixture of thaumasite and gypsum, were found by Mr. A. W. G. Kingsbury in 1956 in a quartz–carbonate vein cutting a quartz-dolerite sill and presented to the Museum. Associated minerals in the vein are dickite, alunite, and zunyite; this appears to be the first British occurrence of alunite and zunyite. P. G. E.

SHORT COMMUNICATIONS

Bolivarite restudied.

Examination of some amorphous aluminium phosphates led the author to check the physical and chemical properties of bolivarite. The mineral was originally described by L. Fernández Navarro and P. Castro Barea,[1] but no further complete study seems to have been undertaken. Bolivarite, to which the formula $Al_2(PO_4)(OH)_3.H_2O$ had been assigned, was not unanimously considered as a really valid species and verification was deemed necessary.[2] In order to provide information that might be useful for discussion, the newly observed data are here published.

The present study has been made on the type material from Pontevedra, Spain, and the obtained results are compared with those earlier reported.

Optics

Very weakly birefringent.	Cryptocrystalline, very weakly birefringent.[1]
A mosaic texture becomes easily visible with the gypsum plate.	Isotropic.[3,4]
$n = 1{\cdot}506 \pm 0{\cdot}001$.	$n = 1{\cdot}493$,[3] $1{\cdot}496$.[4]
Strongly fluorescent with bright green colour.	Strongly fluorescent with blue-green colour.[5]

X-rays

Amorphous.	Amorphous.[3]

Specific gravity

2·04±0·01 (with Berman's microbalance).	2·05.[1]

Chemical composition

	%	Mol. ratios		%[1]	Mol. ratios
Al_2O_3	36·2	0·355	Al_2O_3	44·07	0·432
P_2O_5	24·9	0·175	P_2O_5	34·93	0·246
Loss on ignition ...	39·5*	2·192	H_2O	20·60	1·143
Total	100·6		Total	99·60	
H_2O at 110° C. after 88 hours	25·5				

* Taken as total H_2O.

It can be seen that the ratio $Al_2O_3:P_2O_5 = 2$ is confirmed. The agreement is even better in the new analysis. On the other hand, a serious discrepancy lies in the total water content. The loss of weight at 110° C. is even higher in the recent determination than the total water content

in the original description. One would rather expect that an amorphous mineral, stored in museum conditions, should eventually have lost humidity. An explanation may be that the original analysis was made on more or less dried material.

Referring to the new chemical data, bolivarite can now more satisfactorily be compared with the related amorphous aluminium phosphates, evansite and vashegyite, which, according to the recorded data in the literature, show, respectively, $H_2O \sim 40$ %, $Al_2O_3:P_2O_5$ 2·25 to 3·07, n 1·483 to 1·50, sp. gr. 1·82 to 2·13, and $H_2O \sim 40$ %, $Al_2O_3:P_2O_5$ 1·26 to 1·48, n 1·47 to 1·505, sp. gr. 1·96 to 2·0.

My thanks are due to Prof. J. L. Amorós, Museo de Ciencias Naturales, Madrid, who kindly supplied the type material.

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[1] L. Fernández Navarro and P. Castro Barea, Bol. real Soc. Esp. Hist. Nat., 1921, vol. 21, p. 326.
[2] Dana's System of Mineralogy, 7th edn, 1951, vol. 2, p. 872.
[3] R. L. Manly Jr., Amer. Min., 1950, vol. 35, p. 108.
[4] E. S. Larsen and H. Berman, Bull. U.S. Geol. Surv., 1934, no. 848, p. 49.
[5] W. L. Brown, Univ. Toronto Studies, Geol. Ser., 1933, no. 35, p. 19.

British gold from the Bouglise collection.

Native gold from Cumberland is a rarity, although Calvert in 1853[1] mentions several localities where he collected specimens and makes particular reference to the Goldscoop (Goldscope) mine near Keswick, which was worked from very early times for copper that had a high gold and silver content. However it was not until 1956, when Mr. A. W. G. Kingsbury presented a specimen (B.M. 1956, 410) collected by himself from Grainsgill, that the British Museum possessed any Cumberland gold. Therefore it was with considerable interest that we heard of a specimen labelled 'Cumberland, England' in the collection of Harvard University.

The gold occurs in minute grains and crystals in a quartz gossan with caledonite, linarite, cerussite, and hemimorphite. This specimen (Harvard 100289) originally came from A. E. Foote of Philadelphia, Pennsylvania. It found its way into the collection of Georges de La Bouglise, a French mining engineer who specialized in collecting gold from every possible locality, many of which he had visited personally. In 1911 this collection was sold in Paris to an American mining pro-

moter, A. C. Burrage of Boston, Massachusetts. It was willed conditionally to Harvard University in 1916 and eventually came into their possession in 1948.

In the Bouglise sale catalogue, p. 60, the specimen in question appears as 477: '40 × 50 × 25 [mm.] Or natif, linarite et calédonite. Echantillon d'associations et de localités intéressantes. *Leadhills, Ecosse.*' The change in locality has given rise to some doubt and research but there seems no valid reason why Bouglise should have decided it came from Leadhills rather than Cumberland.

In an attempt to settle this query I have examined material from both localities in the Royal Scottish Museum and the Museum of the Geological Survey as well as in our own collection. Although gold in matrix is known from Leadhills, it is found only in quartz and is more usually alluvial. On the other hand, gold from Cumberland is very rare. Red Gill in the Caldbeck Fells, Cumberland, and Leadhills, Lanarkshire, both produce linarite, caledonite, and hemimorphite but the specimen resembles the material from Red Gill more nearly than that from Leadhills. Also, as we have seen, gold in small quantities was widespread in Cumberland at one time and in fact Calvert records finding gold 'disseminated in small specks' on 'one of the lead ores at Caldbeck Fells'.[2]

The mineral dealers and collectors of Philadelphia and other towns in Pennsylvania had very close connexions with Bryce M. Wright who was himself a dealer and hailed from the north of England. As the original label bears the locality 'Cumberland, England' I think it more than likely that the occurrence was somewhere in the Caldbeck Fells.

Through the generosity of Professor Clifford Frondel, who has also supplied much of the relevant information, the Department of Mineralogy of this Museum has now received the specimen (B.M. 1958, 732) as a gift from Harvard University.

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[1] John Calvert, The Gold Rocks of Great Britain and Ireland . . ., 1853, p. 103.
[2] Loc. cit., p. 106.

Glottalite is chabazite.

IN 1836 T. Thomson[1] described a new species, naming it *glottalite* from a name of the river Clyde, because the dealer he obtained his one specimen from 'found it, I have reason to believe, in the hills behind Port Glasgow'.

He gives its density as 2·18, states that 'when heated in a glass tube it gives out 21¼ per cent. of pure water', and gives an analysis: SiO_2 37·01, Al_2O_3 16·31, Fe_2O_3 0·50, CaO 23·93 (misquoted in Dana, 6th edn, as 13·93), H_2O 21·25, sum 99·00%.

It has been generally assumed that the mineral, of which no further specimen has been reported, was a zeolite, although the $CaO:Al_2O_3$ ratio is impossibly high, even if we suppose the percentages of CaO and Al_2O_3 to have been accidentally interchanged. M. F. Heddle[2] thought it was probably a mixture of edingtonite and harmotome, BaO having been mistaken for CaO (as had happened with Turner's analysis of edingtonite), and noted in support of this idea that the SiO_2 percentages of glottalite and edingtonite are the same: but the water content, which is probably quite reliable, is far too high for edingtonite or harmotome. R. P. Greg[3] re-examined Thomson's specimen and concluded that 'the crystals . . . are without doubt chabasie. Another proof . . . *glottalite* is described by Thomson as containing 21¼ per cent. of water, which is exactly the proper proportion for chabasie.' Greg's conclusion is supported by the densities: glottalite 2·18, chabazite 2·08–2·16, edingtonite 2·69–2·78.

Thomson's specimen is now in the British Museum collection (B.M. 33946); in July 1939 Dr. F. A. Bannister took an X-ray powder photograph, but this has only recently been examined: it shows clearly that Greg was right, for the powder photograph exactly matches that of chabazite from Česka Lípa [= Bohmisch-Leipa], Czechoslovakia (B.M. 44735). The analysis, apart from the water content, is evidently in error.

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[1] T. Thomson, Outlines Min., Geol., Mineral Analysis, London, 1836, vol. 1, p. 328.

[2] M. F. Heddle, Phil. Mag., 1855, ser. 4, vol. 9, p. 181.

[3] R. P. Greg, Phil. Mag. 1855, ser. 4, vol. 10, p. 118; R. P. Greg and W. G. Lettsom, Min. Gt. Britain & Ireland, London, 1858, p. 171.